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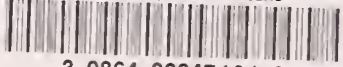
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LOW ENERGY ETHANOL DEHYDRATION  
VIA BARLEY ADSORPTION

*Prepared for*  
**MONTANA DEPARTMENT of NATURAL RESOURCES and CONSERVATION**

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LOW ENERGY ETHANOL DEHYDRATION VIA BARLEY ADSORPTION

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December, 1982

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## Abstract

This investigation evaluated the feasibility of using barley as an absorbant to dehydrate the ethanol-water mixture from distillation to nearly absolute ethanol (99 wt%). Water removal by barley adsorption is energy efficient and applicable to farm-scale facilities. Shabet barley was used and the process variables included: ethanol-water feed composition (55-87 wt%), ethanol-water feed mass flux ( $0.025-0.34 \text{ gm/min-cm}^2$ ), initial grain moisture content (0-2.4 wt%), grain particle size ( $1/32''$ ,  $1/16''$ , and  $1/8''$  hammer-milled), initial adsorption column temperature ( $86-103^\circ\text{C}$ ), adsorption column geometry ( $0.75'' \text{ dia.} \times 12''$ ,  $1.5'' \text{ dia.} \times 14''$ ,  $1.5'' \text{ dia.} \times 24''$ , and  $2.5'' \text{ dia.} \times 23''$ ), grain regeneration (use of the same grain for 5 successive dehydrations), and Shabet barley grain versus Betzes barley straw as an adsorbent. Ethanol dehydration was found to be feasible with a production capacity of about 0.0072 gal 99 wt% ethanol/lb dry barley. Regeneration of the barley by drying reduced its capacity by about 20% and enough ethanol is adsorbed along with the water that the total adsorbed liquid must be recovered during regeneration. The adsorption capacity is independent of the ethanol-water feed composition but the grain should be dry. High temperatures reduce the capacity and are caused by high feed mass fluxes and large-diameter adsorption columns. Smaller grain sizes are preferable and grain has more capacity than straw. The experimental data was used to design a unit to produce 1 gal/hr of 99 wt% ethanol - the size could be incrementally increased for larger production rates. The adsorption column is  $10'' \text{ dia.} \times 10'$ . A grain regeneration (drying) system requires removing the barley from the adsorption column. The bottoms liquid from distillation should provide enough process heat for both adsorption and regeneration.

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## INTRODUCTION

Since the 1974 Arab oil embargo and the ever increasing tensions in the middle east, the United States' need for alternate energy sources has grown tremendously. Ethyl alcohol (ethanol) has long been identified as a possible candidate for the extension of petroleum-based transportation fuels. Ethanol fuels could play an important role in the transition period between today's petroleum fuels and the synthetic fuels of the future.

The idea of using ethanol to supplement petroleum reserves is by no means new. Brazil has been testing different blends of gasoline and ethanol, which is called gasohol, since the 1920's. In 1975 Brazil launched a program to decrease Brazil's dependence on foreign oil. Under this program the average blending level of gasoline is 20 vol% (volume percent) ethanol. In addition to the increased use of gasohol, there has been an increase in the number of pure ethanol driven vehicles.

Gasohol with up to 20 vol% ethanol can be used without any engine modification. Researchers say that optimum blend is 10-15 vol% ethanol.

A major advantage of mixing ethanol with gasoline is that ethanol is an octane booster. Pure ethanol has a research octane number of 106-108. In general, ethanol will increase the octane number of gasoline by 0.5 units for every 1 vol% addition of ethanol. Several oil companies are currently marketing super unleaded gasoline, which is a mixture containing 90 vol% unleaded gasoline and 10 vol% ethanol.

Ethanol can be produced by the fermentation of grains. The starch in the grain is converted into glucose by the addition of an enzyme. A yeast is then

added to convert the glucose into ethanol and carbon dioxide. This is carried out until the ethanol concentration reaches approximately 10 vol%. At that point, the ethanol concentration is so high it kills the action of the yeast.

Ethanol to be used for mixing with gasoline must be nearly anhydrous. A 20 vol% ethanol-gasoline mixture will tolerate only 1 vol% water at 70°F. Simple distillation cannot be used to produce anhydrous ethanol because there is a minimum boiling point azeotrope at 94.4 wt% (weight percent) ethanol. The common method for dehydrating ethanol is called azeotropic distillation. It is a technically-sophisticated process requiring the addition of two more distillation columns and consumes more energy than is contained in the final anhydrous ethanol.

It must be emphasized, when considering the use of distillation in the production of ethanol for fuel, that the majority of the heat required for distillation is the heat needed to concentrate ethanol higher than about 93.5 vol% ethanol in water. Studies have shown that when ethanol is concentrated from 15 vol% to 93.5 vol%, the energy content of the ethanol will be 11 times the amount required for distillation. As higher ethanol concentrations are approached, this ratio drops rapidly and becomes less than 1 at the azeotrope.

As a result of this problem, an alternative to distillation for dehydrating ethanol in the 93.5 to 100 vol% range is needed. In 1979 Purdue researchers reported that in addition to a number of other dehydrating agents, corn was able to remove water from ethanol-water mixtures. It was shown that shelled and cracked corn would concentrate ethanol-water vapors from 77 wt% (weight percent) to 97.7 wt% ethanol (see Table 1 for percent conversions).

The vast availability of barley in Montana makes this grain desirable to use in ethanol production as opposed to the corn used in the Purdue experiments.

Table 1

Ethanol-Water Mixture Data

% Ethanol in Mixture

<u>vol%</u>	<u>wt%</u>	<u>mol%</u>
5	4.0	1.6
10	8.1	3.3
15	12.2	5.1
20	16.5	7.2
25	20.8	9.3
30	25.3	11.7
35	29.8	14.2
40	34.5	17.1
45	39.2	20.1
50	44.1	23.5
55	49.1	27.4
60	54.2	31.6
65	59.4	36.4
70	64.8	41.8
75	70.3	48.0
80	75.9	55.2
85	81.7	63.5
90	87.7	73.6
95	93.7	85.3



Barley is Montana's second largest grain crop; Montana ranks fifth in the United States in barley production. Barley can also be used as a feedstock to produce fermentation alcohol.

The mechanism by which the ethanol dehydration process takes place is selective sorption. In this case, selective sorption means water has a greater affinity for the barley grain than ethanol does and therefore water is sorbed in larger amounts than ethanol, thus dehydrating the ethanol.

In order to understand how this dehydration process occurs, a brief discussion of the sorption phenomenon will be helpful.

### Sorption

There are three types of sorption:

1. Absorption
2. Physical Adsorption
3. Chemical Adsorption

First, adsorption should be distinguished from absorption. Absorption is the bulk penetration of a vapor or gas into the structure of the solid, thus forming a solid solution. Adsorption is the phenomenon where molecules of a gas or vapor will stick to the surface of the solid, but not form a solid solution. The term sorption is used when both processes may occur simultaneously.

Physical adsorption should be distinguished from chemical adsorption, sometimes called chemisorption. Physical adsorption is similar to condensation of a vapor. The gas or vapor is held to the solid surface by van der Waals forces. Chemical adsorption involves the formation of a chemical bond between the solid and the adsorbed liquid. The adsorption of water onto biological materials is almost always physical adsorption.

It is necessary, however, for a sorbed molecule to attach to the solid surface of a sorbent before it can penetrate the field of force between the

molecules of the solid sorbent. Since this is true, adsorption can occur without absorption being present, but absorption must always be preceded by adsorption.

### Physical Adsorption in Packed Beds

The unsteady-state adsorption of gases in packed beds is very common in industry. The main reason for this is their ease of operation and low cost. Adsorption is used in many recovery and purification operations such as: decolorizing mineral and vegetable oils, purifying air, dehydration of gases and vapors, and concentrating of valuable solutes from liquid solutions.

In a packed bed where there is a vapor and strongly adsorbed solute, such as ethanol and water, the vapor enters the packed bed and at first the solid adsorbs the solute rapidly and effectively. The effluent from the bottom of the packed bed is practically solute free (see Figure 1). The distribution of the adsorbate in the solid bed is indicated by the horizontal lines in Figure 1. The bulk of the adsorption takes place over a small adsorption zone, which moves down the column like a wave. The speed of the wave is usually much slower than the linear velocity of the vapor in the column. As the adsorption zone gets closer to the bottom of the column, the concentration of the solute in the effluent starts to rise very rapidly. This is called the break point. Then the concentration of the solute in the effluent rises until it reaches the inlet concentration. The portion of the curve after point C on Figure 1 is called the breakthrough curve.

If the process is highly exothermic a temperature wave will follow the adsorption wave. A rise in temperature of the effluent can be used as an indication of the start of the breakthrough curve.

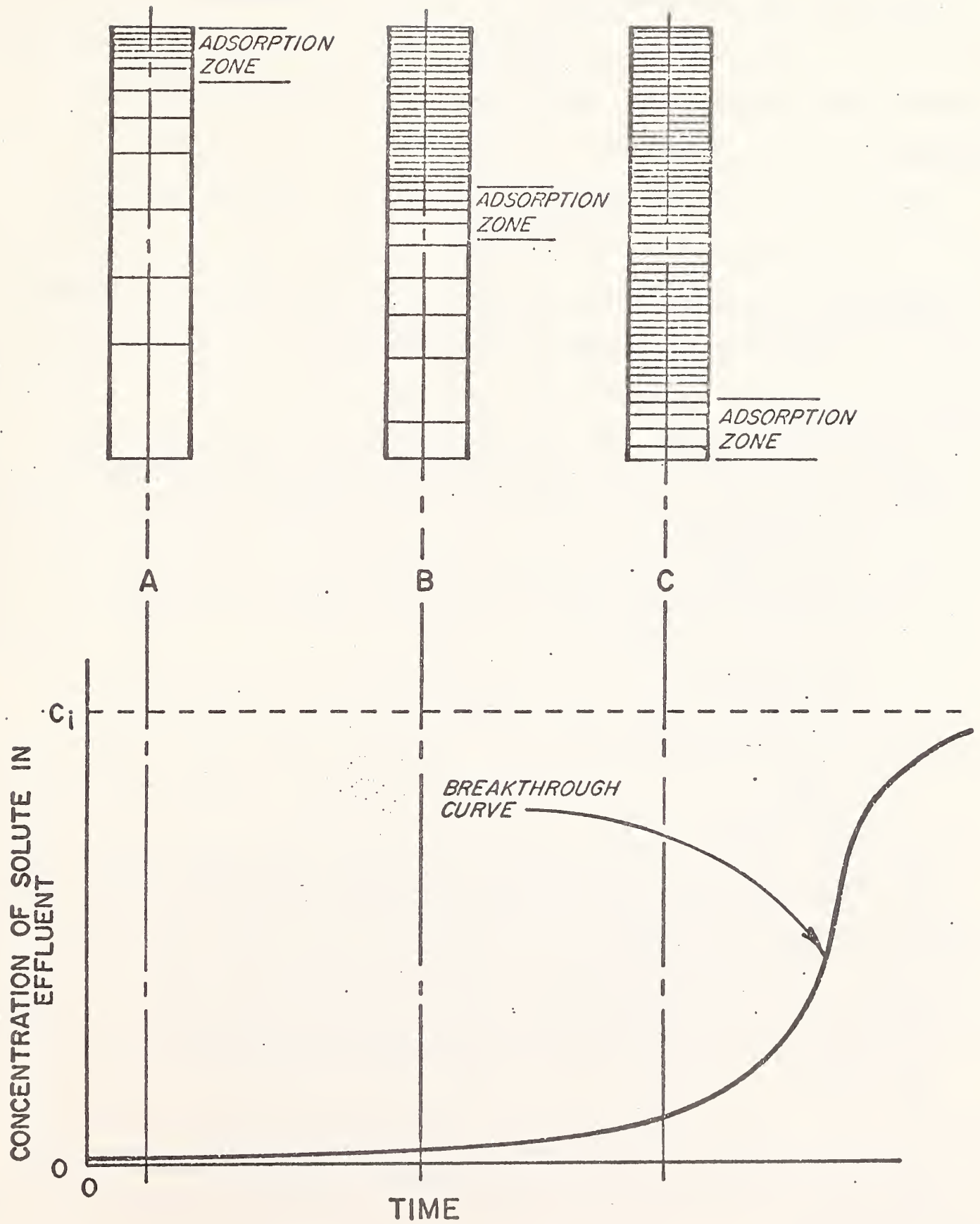


Figure 1. The Adsorption Wave and Breakthrough Curve

## RESEARCH OBJECTIVE

The purposes of this investigation were (1) to determine the feasibility of using barley as an adsorbant to dehydrate ethanol-water mixtures and (2) to develop design data for a farm-scale process unit if the process appeared promising.

## EXPERIMENTAL

The areas to be discussed include process variables, experimental design, criteria for evaluation, and equipment and procedure.

### Process Variables

The following variables were considered important in this investigation:

feed composition

feed mass flux

initial grain moisture

column geometry

multiple grain use

pressure

grain variety

The feed composition to the adsorber is related to the performance of the preceeding distillation column. Commercial distillation units can readily provide 90 wt% ethanol concentrations but farm-scale units will probably be less efficient. These smaller units should readily produce 80 wt% ethanol solutions.

The feed mass flux represents the mass flowrate of feed into the column. The flux is the flowrate divided by the cross-sectional area of the column. Expressing the flowrate as a flux allows columns of different diameters to be easily compared.



The initial grain moisture refers to whether the grain used as the adsorbent is at its "as received" moisture or partially or completely dried prior to its use.

Column temperature has a large effect on adsorption performance as discussed in the Results section of this report. Being an exothermic process, heat given up by adsorption will result in a temperature rise in the column. To keep the process instrumentation simple (consistent with the objective of designing a farm-scale unit) it was decided to control only the initial temperature prior to the introduction of the feed. This temperature should be between the boiling points of the two components: 78°C for ethanol and 100°C for water.

Grinding and separation problems would make it impractical to obtain a narrow range of grain particle sizes. Therefore, it was decided to investigate the particle size distributions that could be produced using a typical hammer mill - some differences could be obtained by using different screen sizes in the mill.

For a given volume of adsorbent (grain), many different combinations of column diameter and length are possible. The diameter must be large enough so that the vapor is evenly distributed across the cross-sectional area of the columns and does not channel up the side; however, as the diameter increases, the area available for heat transfer decreases and the temperature of the column increases due to the heat of adsorption. A larger column length allows a higher percentage of the grain to be used as an adsorbent but has the undesirable result of increasing the pressure drop of the vapor flowing through the column.

The capacity of biological adsorbents such as grain is often decreased when the adsorbent is reused. It is important to evaluate any capacity reduction due to adsorbant regeneration.



Pressure is a possible process variable but was not investigated because operation at ambient pressures (~640 mm Hg) is desirable from a cost viewpoint.

Different barley varieties might have different adsorbant properties but there was only time enough to investigate one variety.

### Experimental Design

There were two distinct sequences of experiments: preliminary experiments and design experiments. The preliminary experiments were chosen to evaluate the feasibility of using barley as an adsorbent and determine the significant process variables. The design experiments were selected to obtain the information necessary to design a farm-scale unit.

### Preliminary Experiments

A central composite experimental design (see Research section) was selected to investigate the effects of feed composition, feed mass flux, and initial grain temperature. This type of experimental design is well suited to the statistical interpretation of data gained while investigating several variables simultaneously and, if the variables are interdependent, provides the data necessary to develop an equation to describe the effects. Most feed compositions were 75, 80 and 85 wt% ethanol with one each at 73 and 87 wt%. Feed mass fluxes were 0.025, 0.140, and 0.250 gm/min-cm<sup>2</sup> except for one at 0.290 gm/min-cm<sup>2</sup>. Initial grain temperatures were 86, 93 and 100°C with one at 103°C.

Three more sets of experiments were run after the central composite design in which only one variable at a time was investigated: grain particle size, initial moisture content of grain, and a comparison of using barley grain and barley straw as adsorbents. After the grain had been ground in a hammer mill having a one-sixteenth inch screen three particular sizes were then separated: 0.208-0.295 mm, 0.589-0.833 mm, and 1.651-2.362 mm. Initial grain moistures

tested were 0 wt%, 1.5 wt%, and 2.4 wt%. The barley grain variety was Shabet and the barley straw variety was Betzes.

### Design Experiments

Based on information gained from the preliminary experiments, design information was obtained by testing combinations of feed mass flux, grain particle size, and adsorption column geometry. The feed mass flux was varied from 0.04 to 0.34 gm/min-cm<sup>2</sup>. Three screens were used in the hammer mill - 1/32", 1/16" and 1/2". The column geometries used were a 1.5" dia. X 14" schd. 40 pipe, a 1.5" dia. X 24" schd. 40 pipe, and a 2.5" dia. X 23" schd. 80 pipe (a 0.75" dia. X 12" schd. 40 pipe had been used for the preliminary experiments). The length:diameter ratios for these columns were 8.7:1, 14.9:1, 9.9:1, and 14.6:1 respectively.

To evaluate grain regeneration characteristics the same grain was used for five consecutive adsorption experiments with the grain being completely dried prior to each run.

### Criteria for Evaluation

Initially, comparisons of runs were based on the water sorbed by the grain from the ethanol-water feed, i.e., gm H<sub>2</sub>O removed/gm grain. However, the water removal was calculated indirectly by making a material balance that included the ethanol-water feed to the extractor, the ethanol-water effluent from the extractor, and the ethanol and water sorbed by the grain. The sorbed ethanol and water had to be estimated by taking two or three small samples of wet grain from the extractor and drying then in an oven - the oven wasn't large enough to dry all of the grain. Because the average liquid content of the small wet grain samples was not exactly the same as that of all of the wet grain in the extractor, the quantities of water and ethanol sorbed by the grain were slightly in error. Therefore, when this data was used to calculate the water sorbed by

the grain the latter figure was not exactly correct although it was adequate for comparing the effects of the process variables.

After the central composite experimental design portion of the preliminary experiments had been completed, it was decided to use the volume of dehydrated ethanol that was produced to compare the different experimental runs; because this quantity can be measured directly it provided a more reliable criterion for evaluation. Although the product for each run could not be analyzed instantaneously to determine the ethanol concentration, it was calculated by combining discrete samples collected throughout the run. At the beginning of a run, the ethanol concentration of the effluent from the adsorber was usually above 99 wt%. As water was removed from the feed stream, the barley in the adsorber would eventually become saturated and ethanol concentration in the adsorber effluent would decrease. This concentration would drop below 99 wt% ethanol and approach that of the feed to the adsorber. If all the effluent from the adsorber was sent to the same container, the concentration in this container would start at 99+ wt% ethanol, but it would begin to decrease as the barley became saturated and at some point would be exactly equal to 99 wt% ethanol. In this project, samples were collected during 5-20 minute time periods, depending on the feed mass flux, and these samples were "mathematically combined." In other words, the amount of ethanol and water was calculated for each sample from the concentration and sample weight, and the total number of samples that would have to be added together to produce 99 wt% ethanol was mathematically computed.

## Equipment and Procedure

### Materials

The Shabet barley was ground in a Bell Model 10 hammer mill, placed in sacks, and stored in a refrigerator at 10°C; after grinding the moisture of

the grain was 7-9 wt%. Prior to each experiment the grain was dried by laying it in large aluminum pans to a depth of 0.5-0.8 cm and placing it in a 110-120°C oven for 72-96 hours. Anhydrous ethanol was diluted with distilled water to the desired concentration. All ethanol concentrations were determined using a gas chromatograph containing a column packed with Poropak R and maintained at 190°C.

### Equipment

The equipment used consisted of five major parts:

1. Feed burette
2. Pump
3. Evaporator
4. Adsorber
5. Condenser

A flow diagram of the complete apparatus is shown in Figure 2.

The glass feed burette was either 50 ml or 100 ml depending on the volume of feed required. The smaller burette was accurate to 0.1 ml and the larger to 0.2 ml.

For some of the preliminary experiments a Model HDB-1-30R Milraynl D positive displacement pump with a maximum capacity of 2 ml/min was used. Because a high pressure pump was not required and due to its uneven flow discharge characteristics, this pump was replaced with a Buchler Model 2-6250 peristaltic pump. The peristaltic pump gave a much more uniform flow rate and, having four pump heads, the flow rate could be adjusted from 0-16 ml/min.

The evaporator, which vaporized the aqueous ethanol, consisted of a one-inch pipe filled with copper-clad BB's. The entire evaporator was wrapped with heating tape and was insulated. It was placed vertically so the aqueous ethanol would enter the top and drop down through the hot BB's. The evaporator was packed with BB's in order to supply a high surface area so complete vaporization could take place. A thermocouple was placed right below the output of the evaporator so the temperature of the exiting vapor could be monitored.



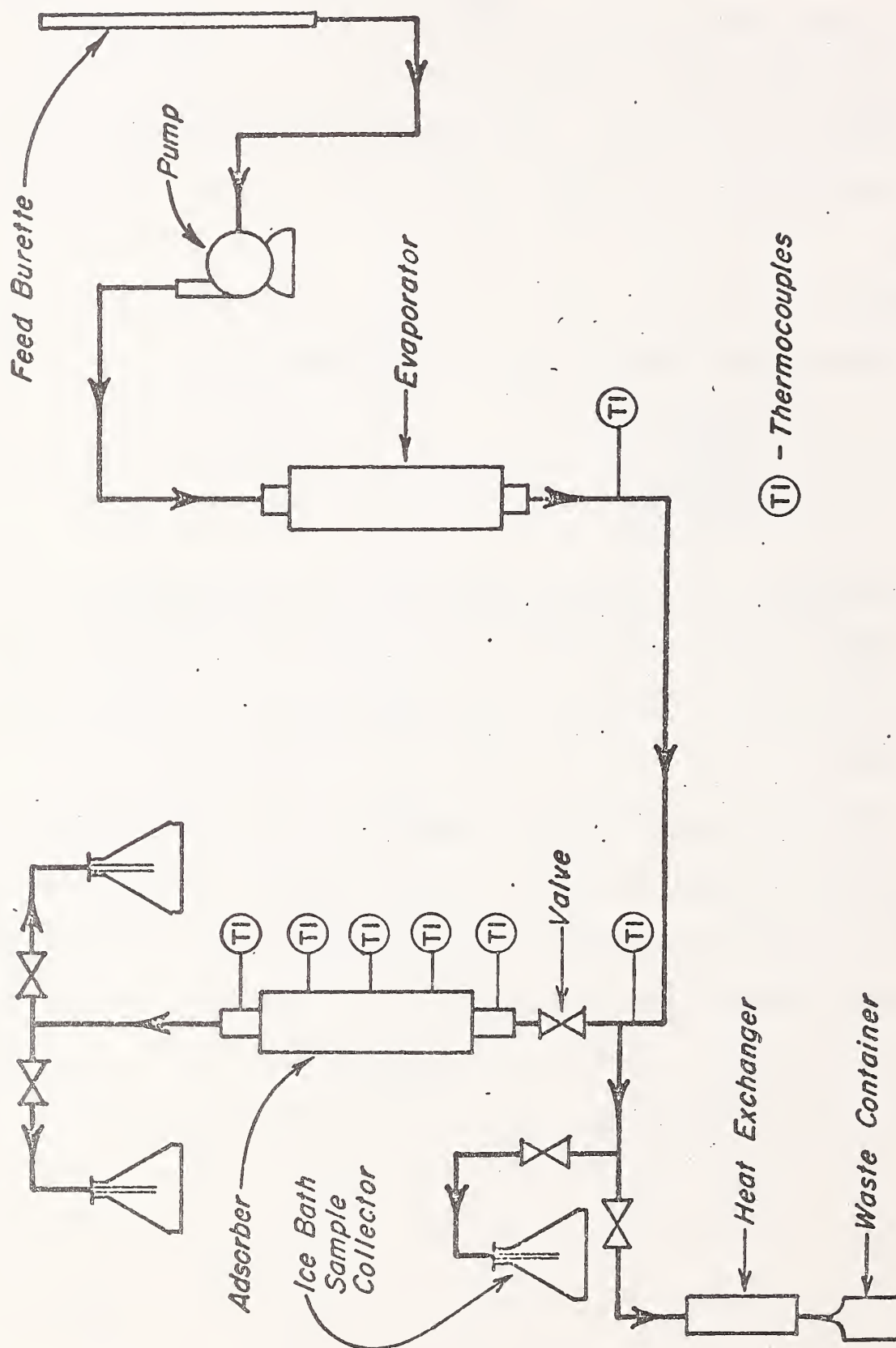


Figure 2. Simplified Flow Diagram of Experimental System



The output of the heating tape for the evaporator and other equipment was controlled by a Powerstat variable transformer.

The adsorbers were fabricated from either copper or black iron pipe. The purpose of the adsorber was to hold the grain in a fixed position. Heating tape was wrapped around the adsorber and the entire adsorber was insulated. One piece of heating tape was used with the 0.75" x 12" and 1.5" x 14" columns. Two separately-controlled pieces of heating tape were used with the 1.5" x 24" and 2.5" x 23" columns. There were thermowells at the entrance, exit, and every 3-4 inches along the adsorption column. Thermowells were inserted so the ends were at the center of the adsorption column. One thermowell was placed at the edge of the column about half way up. The thermowells consisted of 3/16" copper tubing with the ends soldered shut. Thermocouples were pushed into the thermowells as far as they would go.

After the vapor left the adsorber, it entered a water-cooled condenser where the samples were collected in test tubes. The vapor was kept hot until it entered the condenser. This was done in order to prevent the vapor from condensing and dripping back into the adsorption column.

Plastic tubing was used as far as the evaporator. Thereafter any tubing was copper that was traced with heating tape (Powerstats were used to control the temperature of the tubing). All the thermocouples used were chromel-alumel. A Cole-Palmer digital thermometer that was accurate to 1°C was used to indicate temperatures.

#### Procedure

The adsorber was blown out before each run with compressed air to insure that it was clean. Teflon tape was wrapped around the threads of the top and bottom caps. The bottom two screens were put into place and a spring was placed between the screens and the cap. The cap was then tightened. The purpose of the springs was to hold the screens in place.

Barley was weighed on a Mettler balance accurate to within 0.1 gm. The barley (60 gm for the 0.75" x 12" column, 230 gm for the 1.5" x 14" column, 400 gm for the 1.5" x 24" column, and 900 gm for the 2.5" x 23" column) was weighed in a pan and then poured through a funnel placed on the top of the adsorber and the adsorber was filled to within 1 cm of the top. The other two screens were put in place at the top of the column. The top cap was then screwed on and tightened, with the other spring between the cap and the screens.

The adsorber was then fitted into place and the thermocouples connected. The heating tape was connected and turned on. Powerstats were used to control the power input to the heating tape. All six Powerstats, for the six sections of heating tape, were turned on and the system was allowed to warm up for about one hour. During this warm-up period, the adsorber and evaporator Powerstats were adjusted to give a higher heat output than was needed during the actual run. This caused the adsorber and evaporator to heat up to required temperatures more quickly.

When the adsorber temperature had come within about 4°C of the temperature necessary for the run, the adsorber heating-tape Powerstat was turned down to a setting that was estimated to be close to the correct setting. Trial-and-error was then used to zero-in the adsorber Powerstat to a setting at which there was virtually no temperature change in the adsorber with respect to time. After the run began, the adsorber Powerstat was left at the constant temperature setting achieved before beginning the run for the 0.75" x 12" column. For the larger columns the heat of adsorption was usually sufficient to maintain the column temperature and one or more heating tapes could be shut off.

While the adsorber was coming to pre-run steady state, liquid feed was pumped into the evaporator. Vapor-phase feed leaving the evaporator would then by-pass the adsorber and be condensed into the waste container. When the higher flow rates were used (4.5 ml/min and above), the evaporator was not able to

vaporize all the incoming aqueous ethanol. In those cases, the remainder of the aqueous ethanol was vaporized in this section of tubing. Feed continued to flow through this part of the system until steady-state was attained with respect to the temperature and flow rate.

Before the run began, vapor that was going into the waste container was directed instead to enter the pre-adsorber ice bath sample collector. As soon as the feed sample was collected, all valves, except the one at the entrance of the adsorber, were closed and feed vapors would then enter the adsorber. This was the initial start of the run and the time and level of liquid in the feed burette were noted. All seven temperatures were recorded first before, and then after, the run began.

Effluent samples from the adsorber were condensed in the post-adsorber ice bath sample collectors. Samples were collected at various times depending on run conditions. At the beginning of the runs, samples were changed every 10-15 grams. As the ethanol concentration started to drop, 3-4 gram samples were taken. One minute after the burette level was noted, flow of effluent was directed to the other ice bath sample collector. The one minute lag time was consistent for all flow rates. During the one minute lag time, all seven temperatures were recorded.

Deciding when to stop the run was done by analyzing effluent samples with the aid of a gas chromatograph or by observing when the exit temperature started to rise. After the run had been going on for a period of time, the ethanol concentration would decrease from a value close to 100 percent down to a value close to that of the feed. At this point, the barley approached saturation. The equipment was allowed to run for a variable period of time after this, depending upon the conditions and what data was needed.

The run was completed by closing all valves directly connected to the adsorber. This sealed off the adsorber and allowed feed vapor to be directed



to the pre-adsorber ice bath sample collector. Another feed sample was collected at this time and the final burette level was recorded. A feed sample from the pump was taken and the settings of the Powerstats were recorded.

The column was allowed to cool for several hours. Then for the 0.75" x 12" column grain samples were taken from the top and bottom, weighed, and dried. The overall grain moisture content was taken as the average of the two sample moisture contents. As previously mentioned, use of samples to determine the overall grain moisture after adsorption was necessary because not enough oven capacity was available to dry the entire adsorber content for all runs. For the 0.75" x 12" column, a check showed that the averaging approach was within 1 wt% of the overall moisture. When the larger columns were used three samples were taken but the averages were not as reliable and the error correspondingly larger.

## RESULTS AND DISCUSSION

This section will sequentially address the preliminary experiences, the design experiments, and the general observations about the process.

### Preliminary Experiments

The primary purpose of these experiments was to determine if barley would be a feasible adsorbant for ethanol dehydration. In addition, the principal process variables were investigated to select those which are most important to the dehydration process. These experiments were grouped into the following categories:

- effects of temperature, feed mass flux, and feed composition

- effects of grain particle size

- effects of initial moisture content of grain

- comparison of grain and straw

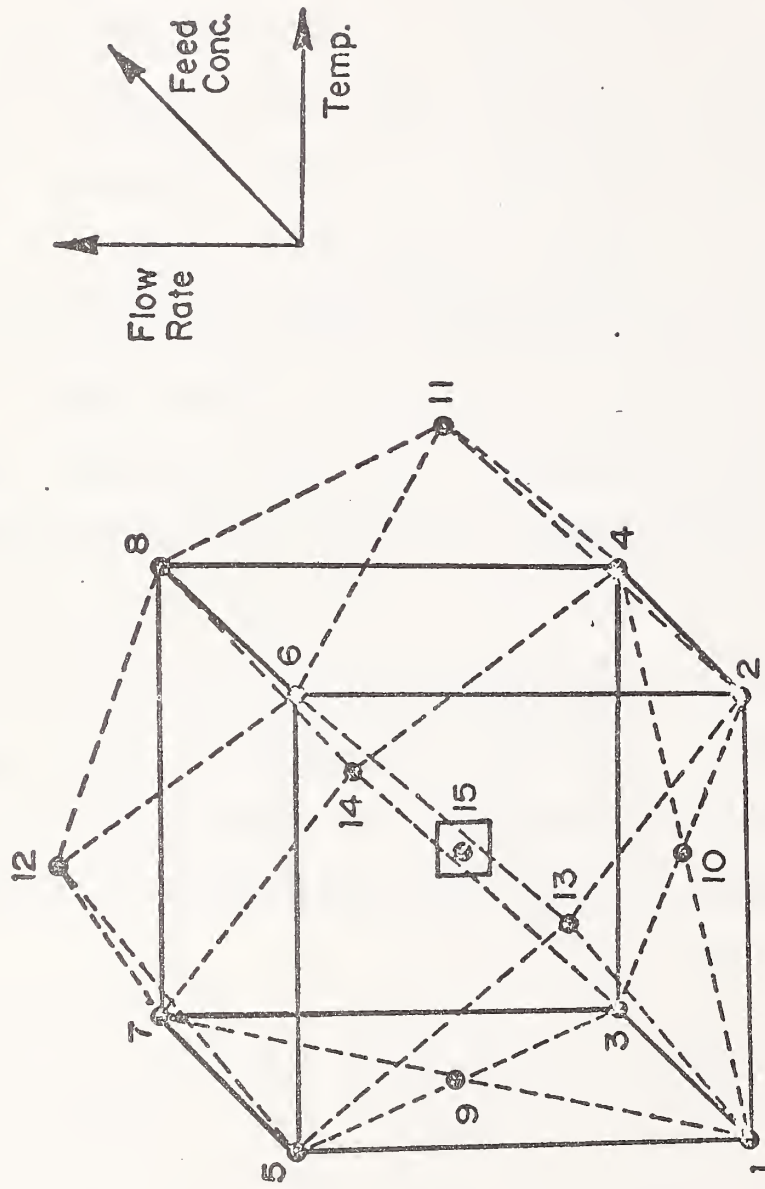
### Effects of temperature, feed mass flux, and feed composition

As previously mentioned, the experiments (runs) used to investigate these variables were arranged according to a central composite experimental design. A graphical representation of this design is shown in Figure 3; specific variables values and 99 wt% ethanol yields for each run are summarized in Table 2.

Figure 4 shows a plot of water removal for 99 wt% ethanol as a function of initial grain temperature. Runs 26, 30, and 50 had a constant feed composition of 76.5 wt% ethanol and feed mass flux of  $0.025 \text{ gram/minute-centimeter}^2$  ( $\text{gm/min-cm}^2$ ). The initial temperature was the only parameter that was varied. Runs 40, 41, 43, 44 and 46 had a different set of constant values: the feed mass flux for these runs was  $0.14 \text{ gm/min-cm}^2$  and the feed composition was 81.0 wt% ethanol. Here again, the only variable was the initial temperature of the grain. It can be seen that for both constant sets of feed mass flux and feed composition, the water removal is inversely related to the initial temperature. This seems reasonable when considering that as the temperature of a liquid increases, its vapor pressure increases, which seems likely to cause any adsorbed liquid to be released from the barley.

Figure 5 shows a plot of water removal for 99 wt% ethanol as a function of feed mass flux. Here, Runs 26, 28, and 50 were held constant at an initial temperature of  $86^\circ\text{C}$  and feed composition of  $\sim 77.0 \text{ wt\% ethanol}$  while the feed mass flux was varied, and Runs 41, 45, and 47 were held constant at an initial temperature of  $93^\circ\text{C}$  and feed composition of  $\sim 81.5 \text{ wt\% ethanol}$  while the feed mass flux was varied. Note that for the conditions used, the amount of water sorbed is inversely related to the feed mass flux. This decrease in water removal capability as the mass flux increases is related to the effect of temperature that has just been discussed. The process of adsorption releases heat and causes the temperature of the grain to increase. Observations showed





not to scale

Figure 3. Graphical Representation of Central Composite Design

Table 2

Central Composite Design

Point No.	Run No.	Initial Temp. (°C)	Feed Mass Flux (gm/cm <sup>2</sup> -min)	Approx. Feed Conc. (wt% ethanol)	99 wt% Ethanol Yields	
					Water Removal (gm H <sub>2</sub> O sorbed/gm grain)	Ethanol Dehydration (ml ethanol/gm grain)
1	26, 50	86	.025	75	0.0838, 0.0755	0.326, 0.302
2	30	100	.025	75	0.0328	0.132
3	37	86	.025	85	0.0432	0.318
4	38	100	.025	85	0.0262	0.202
5	28	86	.250	75	0.0146	0.0555
6	39	100	.250	75	0.0099	0.0302
7	36	86	.250	85	0.0076	0.0405
8	33, 39	100	.250	85	0.0104, 0.0103	0.0602, 0.0728
9	44	86*	.140	80	0.0165	0.0842
10	47	93	.025*	80	0.0309	0.169
11	43	103	.140	80	0.0113	0.0587
12	45	93	.290	80	0.0121	0.0528
13	48	93	.140	73	0.0190	0.0640
14	49	93	.140	87	0.0105	0.0942
15	40, 41, 46	93	.140	80	0.0144, 0.0137, 0.0142	0.0708, 0.0725, 0.0721

\*Lower Limit

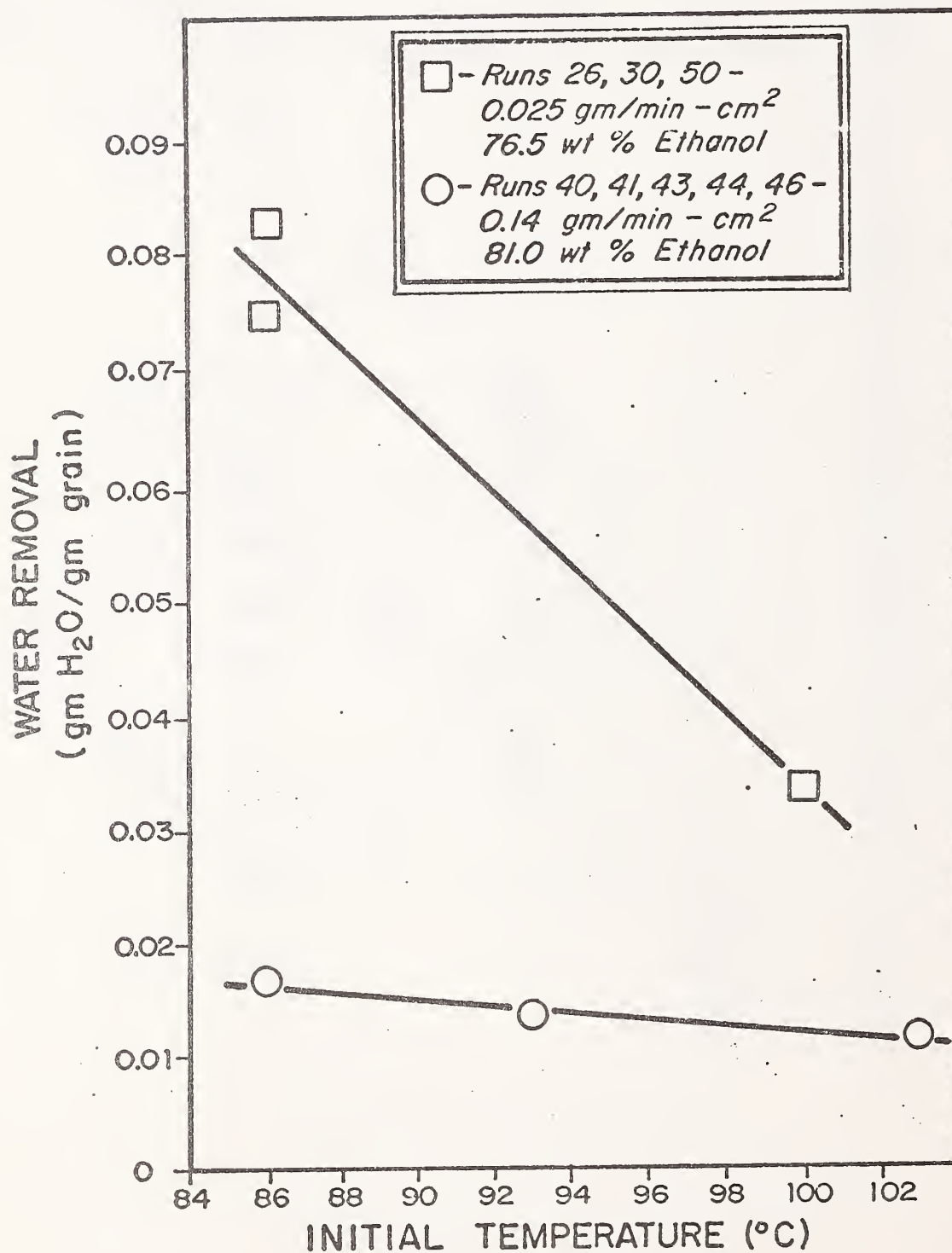


Figure 4. Water Removal vs. Initial Temperature for 99 wt% Ethanol

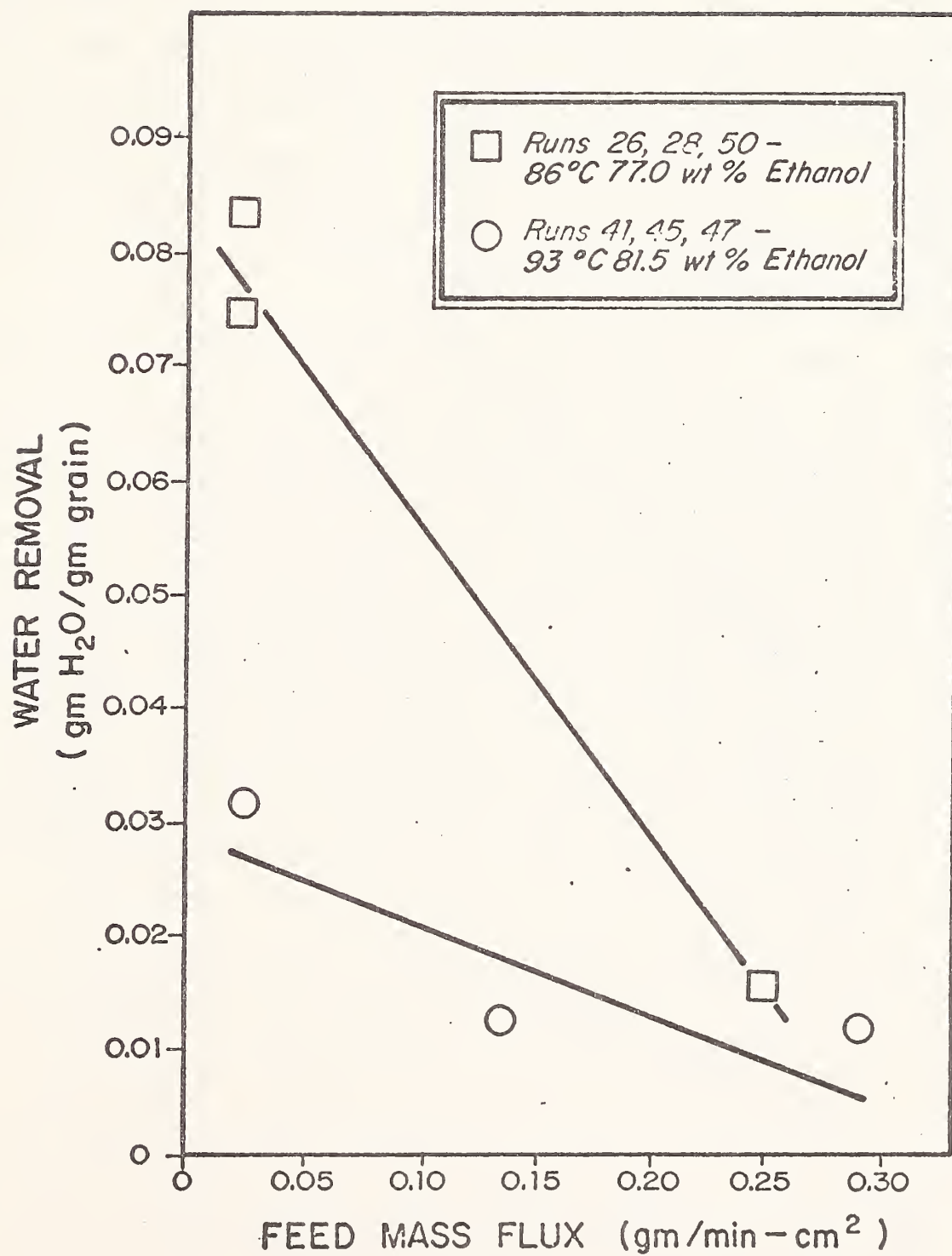


Figure 5. Water Removal vs. Feed Mass Flux for 99 wt% Ethanol

that the temperature of the grain inside the adsorption column increased about  $1^{\circ}\text{C}$  with a low feed mass flux of  $0.025 \text{ gm/min-cm}^2$  (Run 26) and about  $10^{\circ}\text{C}$  with a high flux of  $0.250 \text{ gm/min-cm}^2$  (Run 28); the initial grain temperature was  $86^{\circ}\text{C}$  and the feed concentration was 75 wt% ethanol for both runs. Because more water was available for adsorption at the high feed mass flux more heat was generated than for the low feed mass flux. This caused the increase in grain temperature to be large at the high feed mass flux and reduce the water removal capacity of the grain.

Figure 6 shows a plot of water removal for 99 wt% ethanol as a function of ethanol feed concentration. Here, Runs 26, 37, 50, and 53 were held constant at an initial temperature of  $86^{\circ}\text{C}$  and feed mass flux of  $0.025 \text{ gm/min-cm}^2$  while the ethanol feed concentration was varied, and Runs 46, 48, and 49 were held constant at an initial temperature of  $93^{\circ}\text{C}$  and feed mass flux of  $0.14 \text{ gm/min-cm}^2$  while the ethanol feed concentration was varied. Although Run 53 was not part of the central composite design, with a 55 wt% ethanol content it was used to show how feed ethanol concentrations lower than 75 wt% ethanol affected the amount of water sorbed. It can be seen here that the amount of water sorbed is inversely related to the ethanol feed concentration. This would seem to be reasonable since a decrease in the ethanol feed concentration corresponds to an increase in water feed concentration. Therefore, the amount of water sorbed is actually directly related to the water feed concentration. Since the concentration of water in the feed is the main driving force for sorption of water, it would seem reasonable that an increase in the water concentration in the feed would increase the amount of water sorbed.

Data from Runs 26-50 (excluding 34 and 35) was used to develop a correlation for the yield of 99 wt% ethanol per gram of grain with respect to initial temperature, ethanol feed concentration, and feed mass flux. Feed ethanol



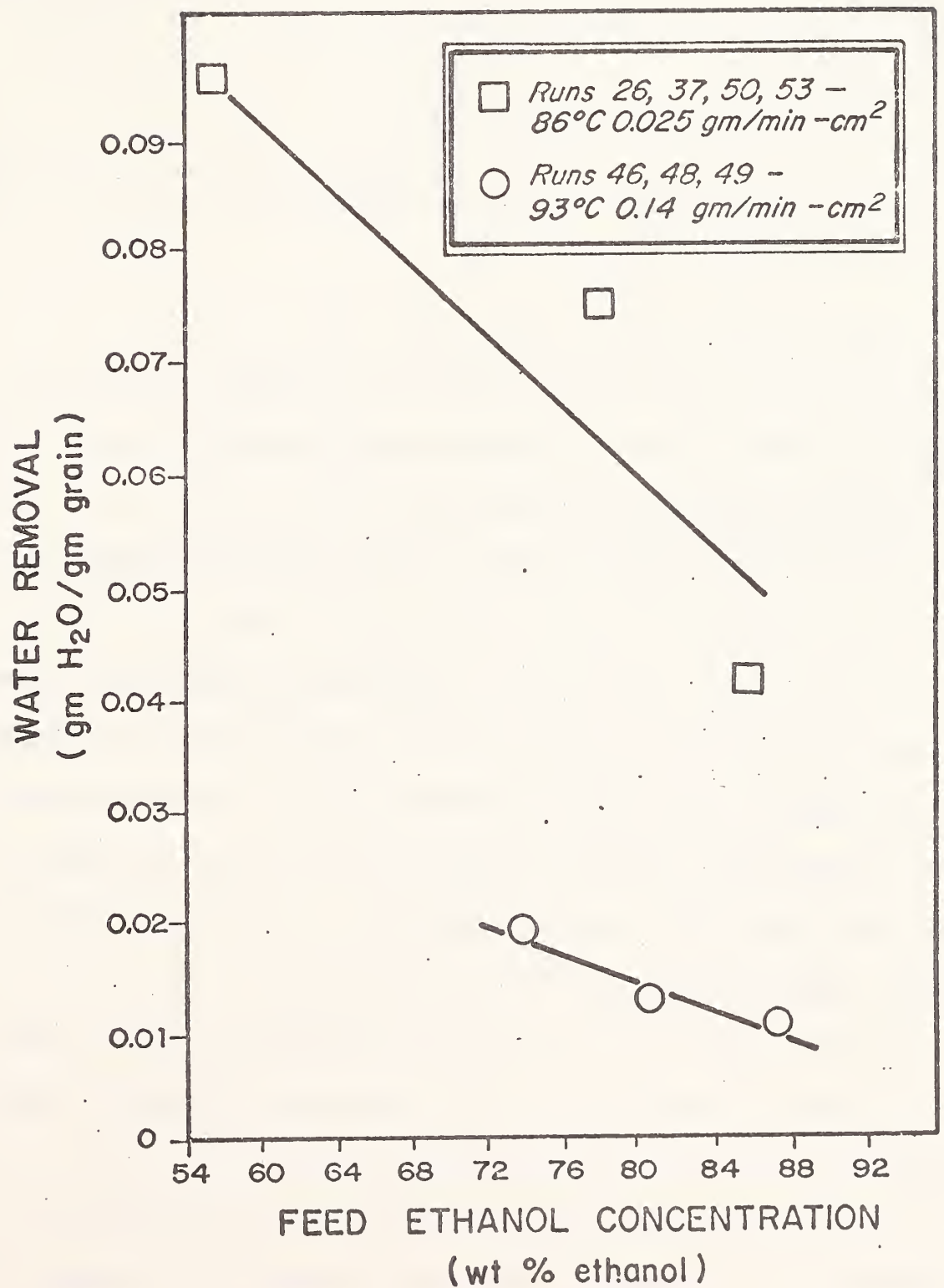


Figure 6. Water Removal vs. Feed Ethanol Concentration for 99 wt% Ethanol

concentration was found to be statistically insignificant; therefore it was not included in the correlation. A statistical regression technique (stepwise forward elimination) was used to develop the form of the equation and an optimization technique (Complex Method of Box) was used to evaluate the constants resulting in:

$$C = 0.0729 / ((T-80)^{0.529} F^{0.6439})$$

C = milliliters of ethanol concentrated per gram of barley for a combined sample of 99 wt% ethanol

T = initial temperature (°C)

F = feed mass flux (gm/min-cm<sup>2</sup>)

The R-squared value for the correlation is 0.88; this indicates a very strong correlation in that about 88% of the variability in ethanol dehydration data is explained by the above equation.

This correlation shows that the amount of ethanol concentrated had an inverse relationship with respect to the initial temperature and the feed mass flux. During earlier discussions, it was noted that the amount of water sorbed was also inversely related to the initial temperature and the feed mass flux. Since the process by which the ethanol was concentrated was by having water removed from the feed stream, it seems reasonable that the amount of ethanol concentrated should have similar relationship to the initial temperature and feed mass flux as the amount of water sorbed does.

A probable explanation of why the feed composition had no effect on the amount of ethanol concentrated for the experiments performed is that as the feed ethanol concentration increased, there was less water that needed to be removed in order to concentrate the same amount of ethanol. Earlier it was noted that as the feed ethanol concentration increased, the amount of water sorbed decreased. Therefore, as the feed ethanol concentration increased, the amount of water sorbed decreased but the amount of water that needed to be

sorbed also decreased. It would appear, then, that these two effects cancelled each other out.

#### Effects of grain particle size

Figure 7 shows the effect that grain particle size had on ethanol dehydration. It can be seen that the largest particle size did not work as well as the two smaller particle sizes. This seems reasonable since the largest particle size would not have had as much surface area for adsorption of water as the smaller particles did.

It can be seen that Runs 56 and 57 had similar results. One possibility was that the ethanol dehydration was not dependent upon the barley particle size with particles smaller than those used in Runs 56 and 57. Another possibility was that the data for these two runs contained too much experimental error to make any conclusions with respect to particle size for this particle size range.

#### Effect of initial moisture content of grain

Figure 8 shows the effect that the initial moisture content of the grain had on ethanol dehydration. It can be seen that as the initial moisture content was increased, the amount of ethanol dehydration decreased. This seems reasonable since the grain will only sorb a specific amount of water for a given set of conditions and, if there was water in the grain before the run began, there was that much less room for additional water.

#### Comparison of grain and straw

A comparison between water removal using dried barley straw (Betzes) and dried barley grain (Shabet) showed 0.0290 gm water/gm straw and 0.0432 gm water/gm grain. The initial temperature was 86°C and the feed mass flux was 0.025 gm/min-cm<sup>2</sup> for both runs. The feed concentration with the straw was 83.0 wt% ethanol while it was 85.5 wt% ethanol with the grain. If these

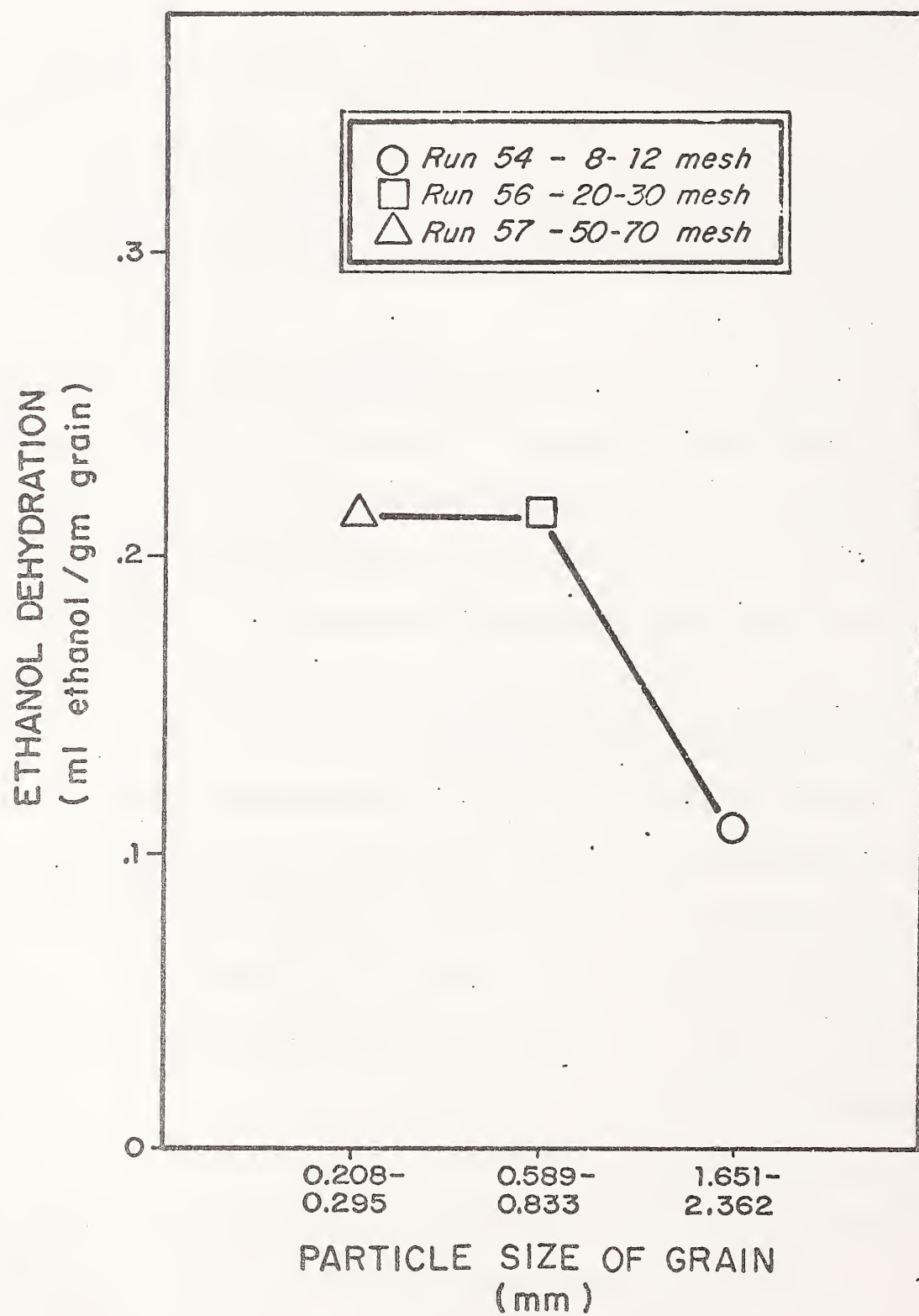


Figure 7. Ethanol Dehydration Capacity vs. Grain Particle Size for 99 wt% Ethanol



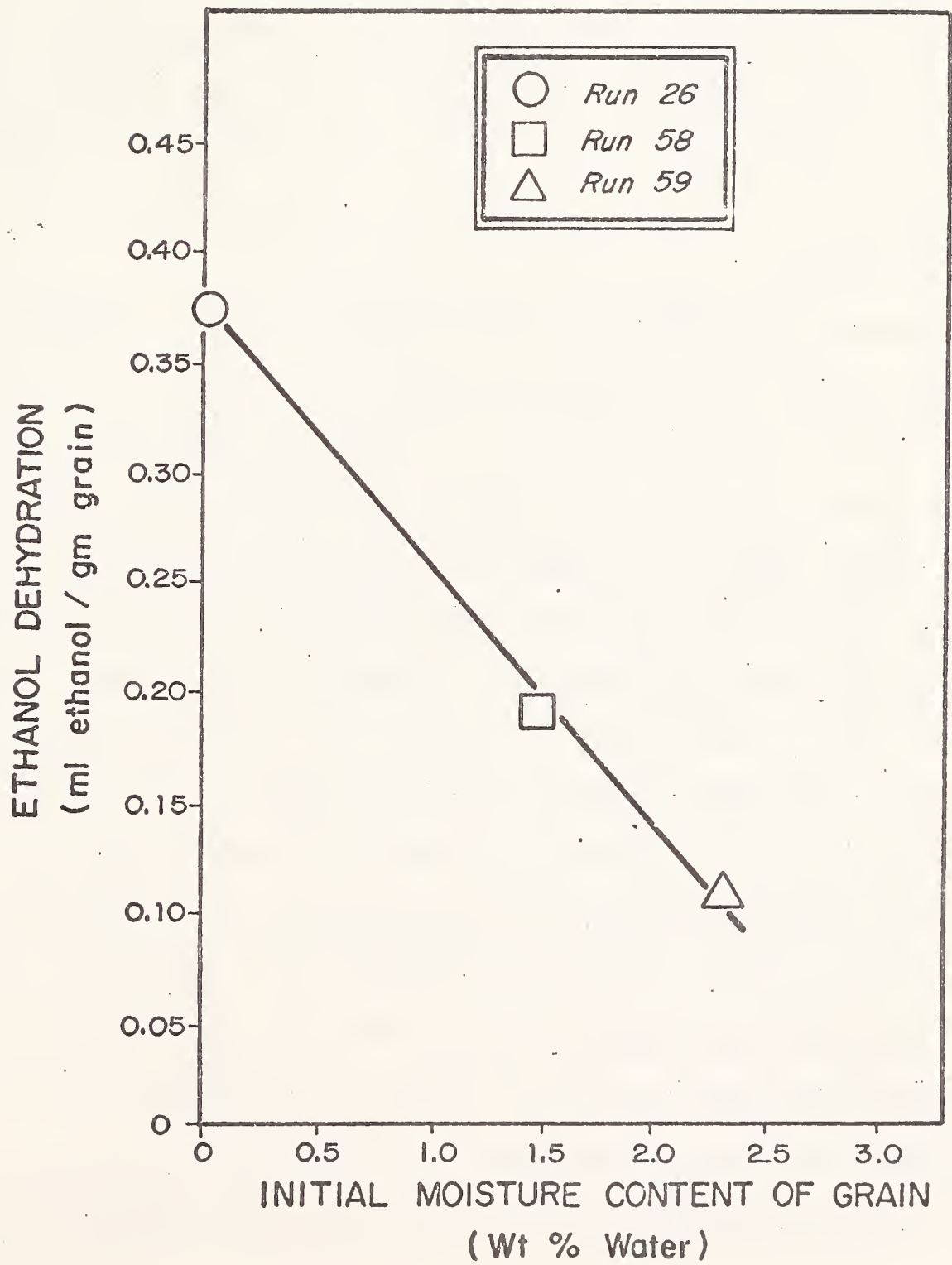


Figure 8. Ethanol Dehydration Capacity vs. Initial Moisture Content of Grain for 99 wt% Ethanol

concentrations had been the same, the difference in results would have been even greater. Earlier researchers have shown that cellulose hygroscopicity had very little variability with respect to its origin (what plant it was from). Therefore, even though the barley straw, which is largely cellulose, did not originate from the same barley species that the grain did, it seems reasonable to assume that Shabet barley grain would give much better results than Shabet straw would.

### Design Experiments

The preliminary experiments had indicated that ethanol dehydration was independent of the feed concentration and should use dry grain at low temperatures. Therefore, a feed concentration of 75 wt% (54 mol%) ethanol was selected as being readily attainable from farm-scale distillation units. The lowest initial grain temperature consistent with maintaining a vaporized feed was 84-86°C. However, more experimental data was required before a farm-scale adsorption unit could be designed. It was particularly important to determine how the adsorption column geometry (diameter and length) would affect ethanol dehydration. Also, because of the significant effect of grain particle size on dehydration, it was necessary to evaluate the different particle size distributions that could be obtained by changing screen sizes in a typical hammer mill. Finally, because a grain drying system would be required to dry the grain before its initial use, an evaluation was made of the possibility of using the same batch of grain many times by regenerating it with drying after using it for ethanol dehydration. The experimental categories were:

- effects of feed mass flux, grain particle size, and adsorption column geometry

- effect of grain regeneration

### Effects of feed mass flux, particle size, and adsorption column geometry

Figures 9, 10, and 11 show ethanol dehydration as a function of feed mass flux and grain particle size for the 1.5" x 14", 1.5 x 24", and the 2.5" x 23" adsorption columns respectively. The equations for the lines shown on the figures are listed in Table 3. The equations were obtained by multiple regression. All but one equation was found to be linear in reciprocal mass flux. The yields for the 1/32" hammer-milled barley were highest at all conditions. The yields for the 1/8" and 1/16" hammer-milled barley were very close to each other in all cases. The results for the 1/8" and 1/16" hammer-milled barley were so similar for the 1.5" x 24" column that one equation was found to represent both particle size distributions.

This similarity between 1/8" and 1/16" hammer-milled barley was due to how close the two particle size distributions were to each other. Figure 12 is a plot of percent of the total weight of barley screened versus pan number for the three particle size distributions. The screen sizes for the various pans are shown in Table 4.

Figures 13, 14, and 15 show ethanol dehydration as a function of feed mass flux and column geometry for the 1/32", 1/16", and the 1/8" hammer-milled barley respectively. The only consistent effect of column geometry was with the 1/32" hammer-milled barley - the ethanol yields from the 2.5"-dia. x 23" column were always less than those of the 1.5"-diameter columns. Generally the smaller-diameter columns gave better ethanol yields at low feed mass fluxes - this effect disappeared above a mass flux of about  $0.1 \text{ gm/min-cm}^2$  for the 1/16" hammer-milled barley and above a mass flux of about  $0.2 \text{ gm/min-cm}^2$  for the 1/8" hammer-milled barley.

The increase in adsorption column length had little effect on the yield. The increase in adsorption column diameter decreased the yield by 20-30% at

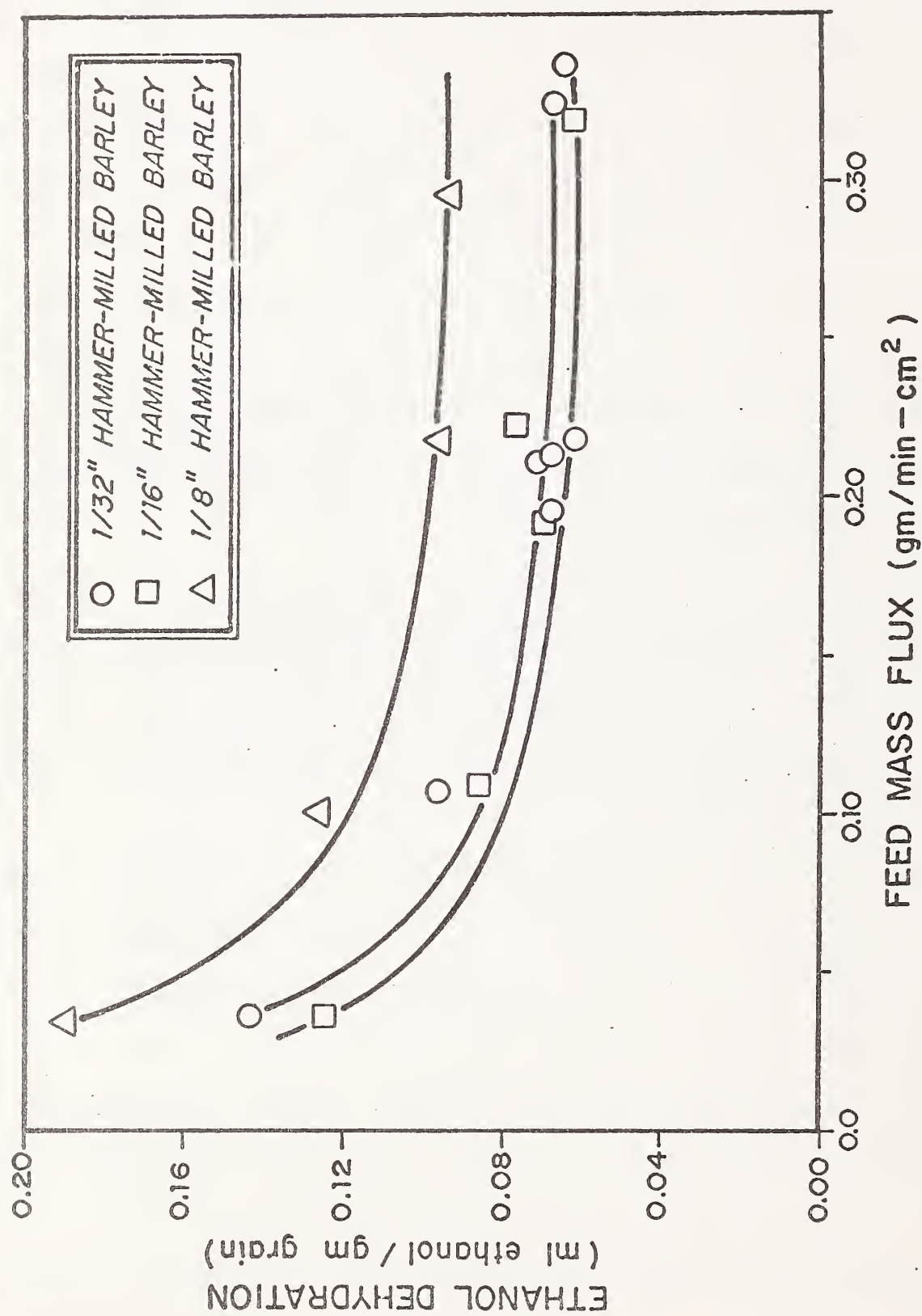


Figure 9. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using the 1.5" X 14" Adsorption Column



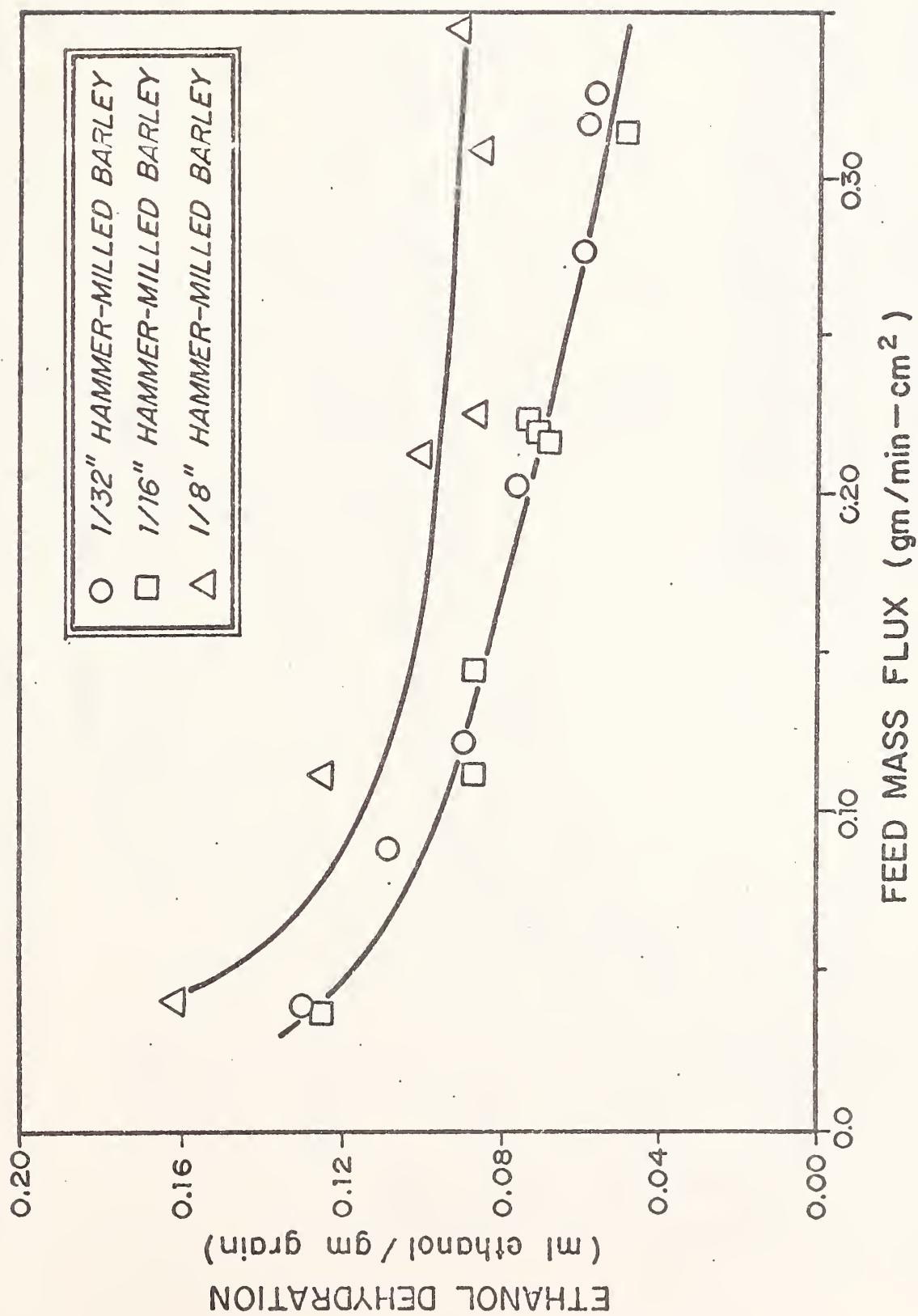


Figure 10. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using the 1.5" X 24" Adsorption Column

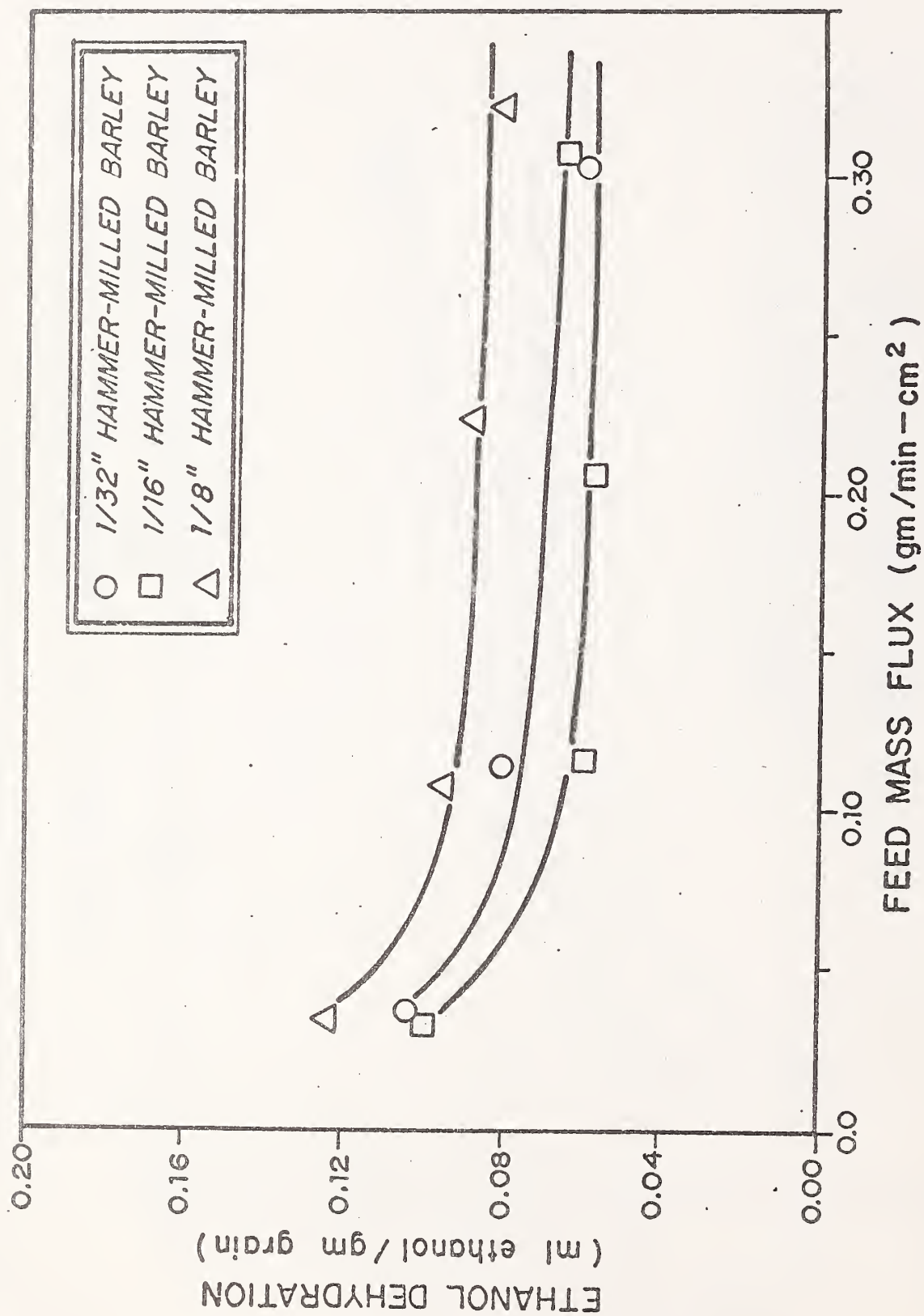


Figure 11. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using the 2.5" X 23" Adsorption Column

Table 3

Equations for Ethanol Dehydration as a Function of Feed Mass Flux  
for the Various Adsorber Columns and Grain Particle Size Distributions

Column Geometry	Grain Size Distribution	Ethanol Dyhydration (gm 99 wt% ethanol/gm grain)
1.5"x14"	1/8"	$Y=0.00242/F + 0.0572$
	1/16"	$Y=0.00348/F + 0.0536$
	1/32"	$Y=0.00407/F + 0.0840$
1.5"x24"	1/8" & 1/16"	$Y=-0.054F + 0.00121/F + 0.10$
	1/32"	$Y=0.00328/F + 0.081$
2.5"x23"	1/8"	$Y=0.00144/F + 0.0523$
	1/16"	$Y=0.00162/F + 0.0599$
	1/32"	$Y=0.00155/F + 0.0786$

\* F = Feed Mass Flux (gm/min-cm<sup>2</sup>)

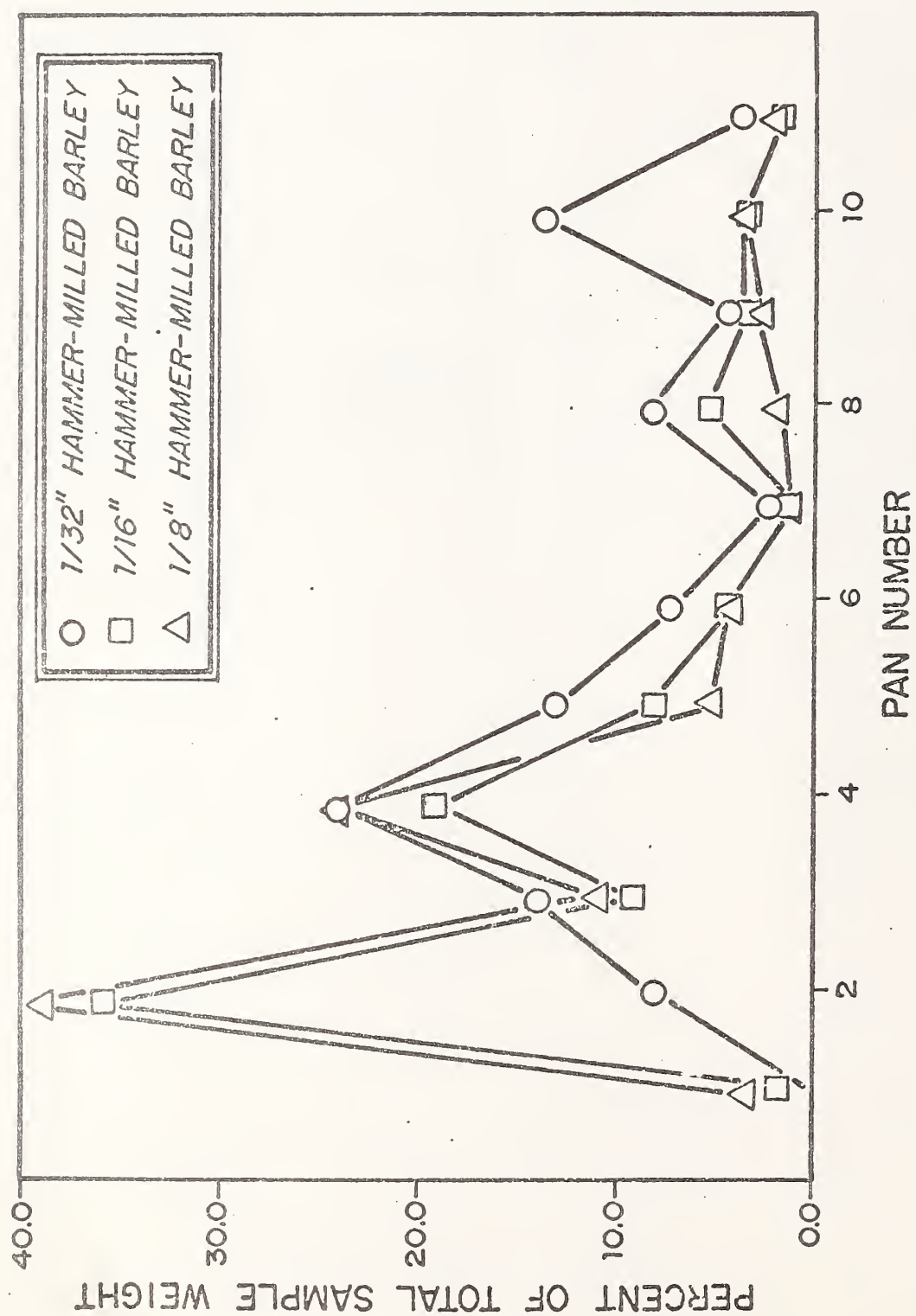


Figure 12. Graphical Representation of the 1/32", 1/16", and 1/8" Hammer-milled Barley Particle Size Distributions



Table 4

The Particle Size Distribution of the 1/8", 1/16", and 1/32"  
Hammer-milled Barley

Screen Number	Screen Size (U. S. mesh)	Screen Opening (mm)	(1/8" hammer-milled barley)	Percent of Total Sample (1/16" hammer-milled barley)	(1/32" hammer-milled barley)
1	10	2.0	3.25	1.7	0.0
2	18	1.0	38.75	36.4	8.2
3	30	0.589	10.4	9.2	14.2
4	40	0.417	24.7	19.7	24.7
5	50	0.297	4.9	8.2	13.9
6	60	0.246	4.5	4.4	7.0
7	70	0.210	1.6	1.4	2.0
8	100	0.147	5.2	5.4	7.8
9	140	0.106	2.4	3.0	4.0
10	200	0.075	3.3	3.1	13.3
11	270	0.053	3.3	3.2	3.0
12	bottom	-	1.7	1.1	1.9

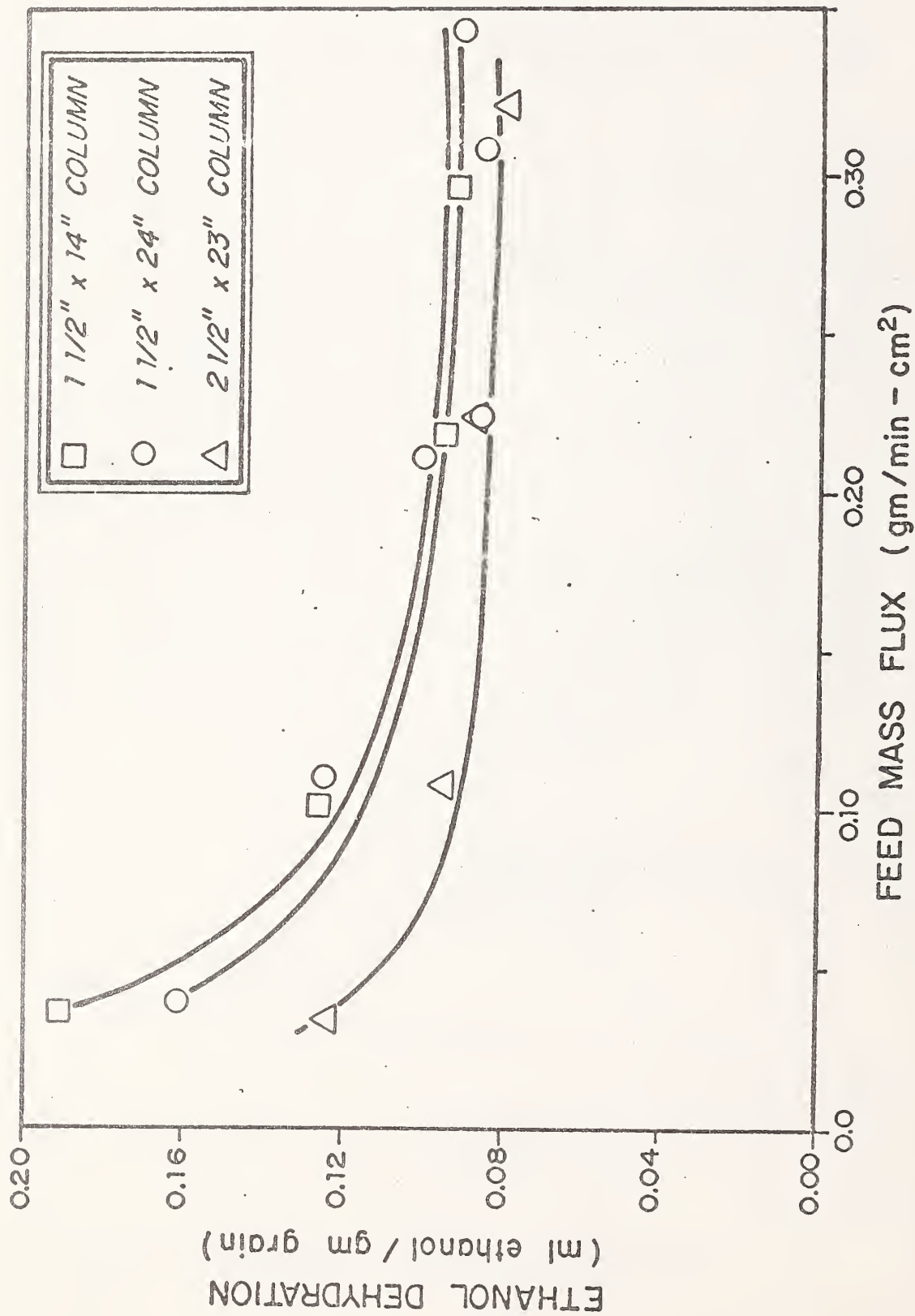


Figure 13. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using 1/32" Hammer-milled Barley

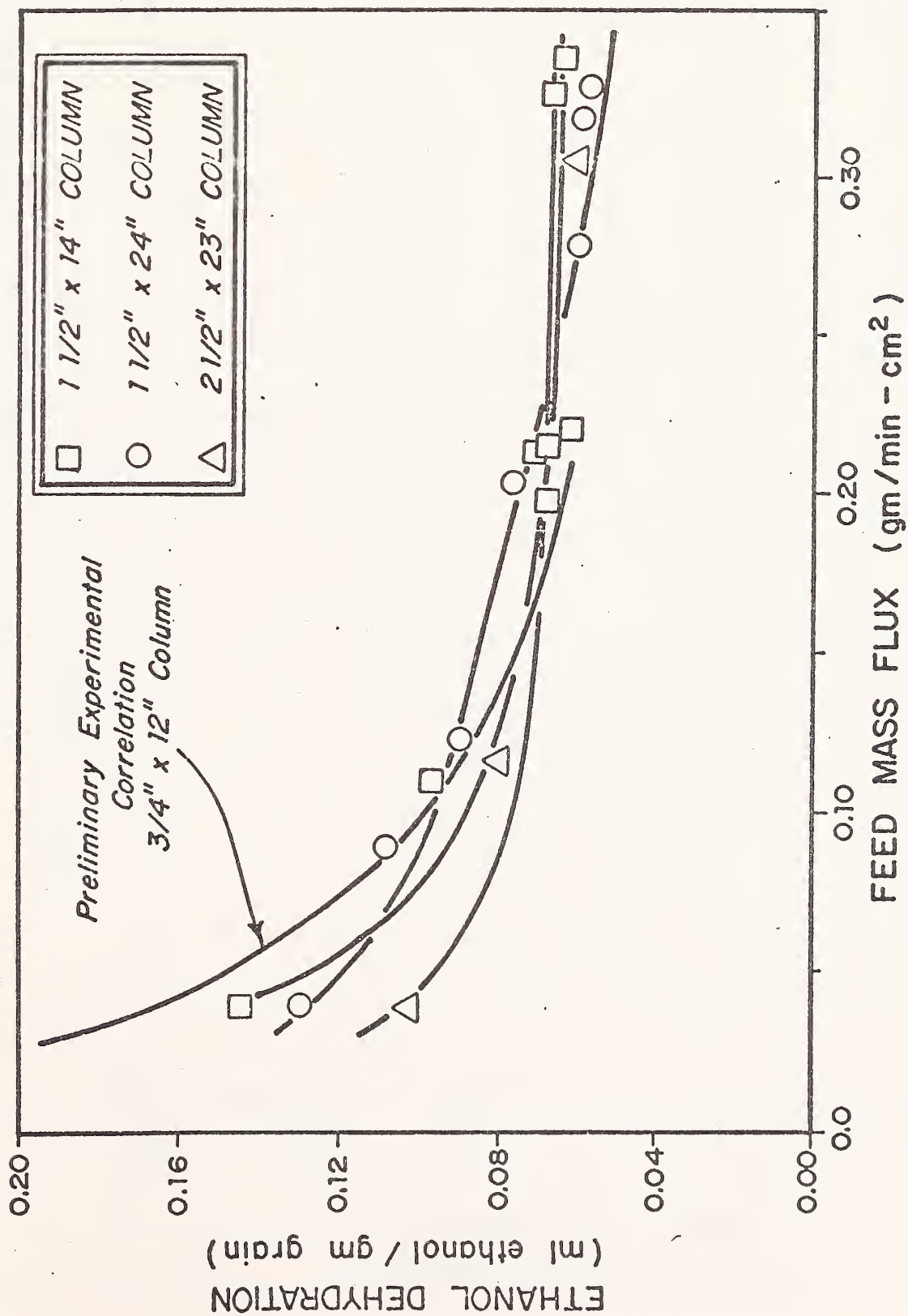


Figure 14. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using 1/16" Hammer-milled Barley

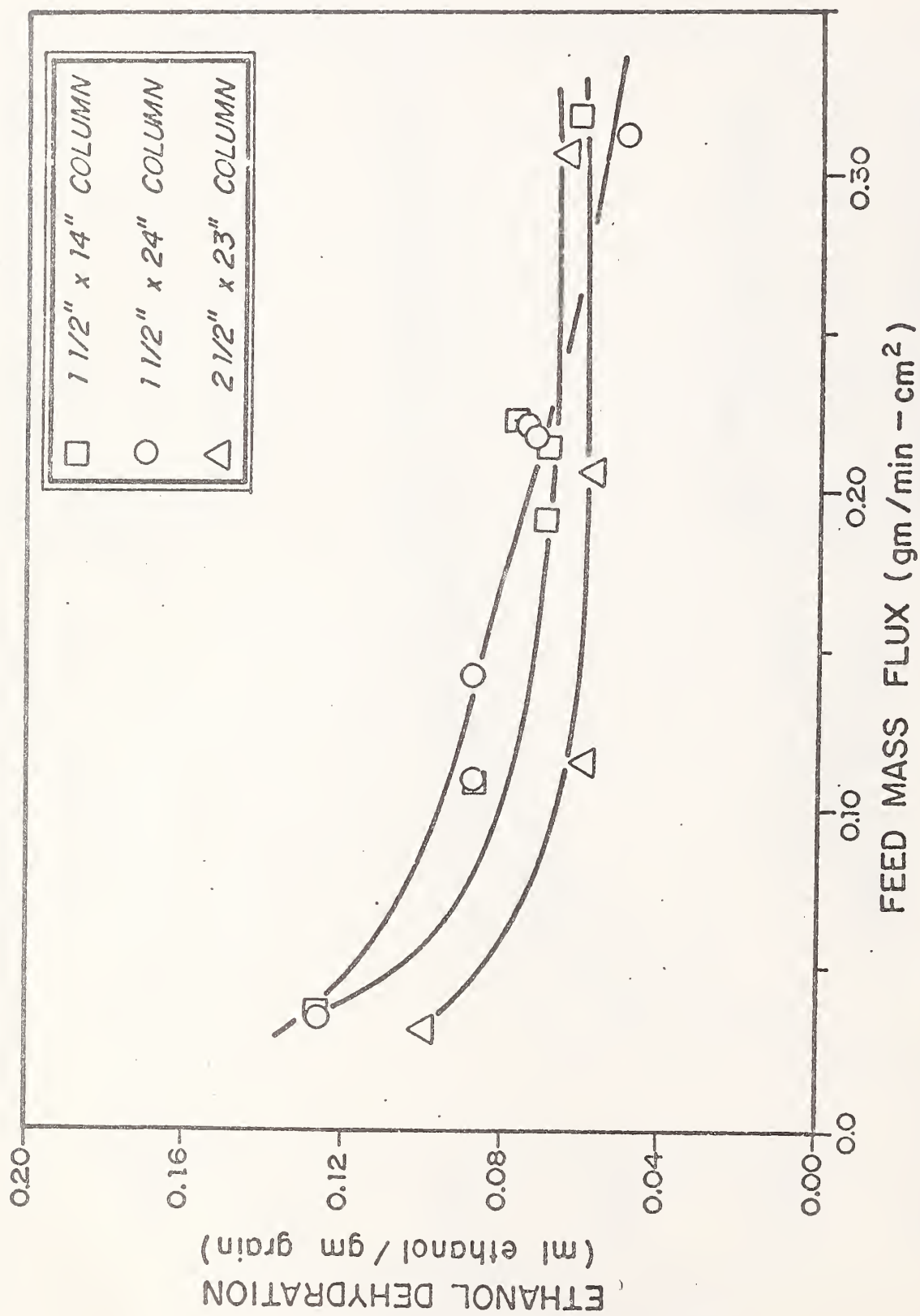


Figure 15. Ethanol Dehydration Capacity vs. Feed Mass Flux for 99 wt% Ethanol Using  $1/8''$  Hammer-milled Barley



the low mass fluxes. This could be due to the increase in temperature in the larger diameter column.

The curve obtained from the preliminary experiments is plotted on Figure 14. It represents a 0.75" x 12" adsorption column. The yields were considerably higher at the low mass fluxes, but the yields dropped off very fast and were about the same as the other yields at the high mass fluxes.

#### Effect of grain regeneration

A total of five runs were made with the same 1/32" hammer-milled barley. All the runs were made with a mass flux of  $0.32 \text{ gm/min-cm}^2$ . This mass flux was chosen because a small variation in flow would not effect the yield. All the runs were made with the 1.5" x 24" adsorption column.

A plot of yield versus number of runs is shown in Figure 16. Initially the yield dropped 20%, then the yield stayed at a constant 0.075 ml 99 wt% ethanol/gm dry barley over the next four runs.

A possible explanation for the decrease in ethanol dehydration capacity might be due to the drying of the grain. A run was made with grain that had been dried for a period of 500 hours in the oven at a temperature of  $110^\circ\text{C}$ . The results of this run were about 20% lower than the value obtained from another run with identical conditions except that the barley had been dried for only 100 hours. It could be possible that the regeneration did not effect the sorptive capacity, but the time it spent in the oven was the cause of the decrease in sorptive capacity. Earlier investigators had found that severe desiccation can reduce the ability of starches to adsorb water. It has been proposed that the hydroxyl groups present in starches play an important role in water sorption. The high heat required to dry the barley could cause mutual bonding of the hydroxyl groups, thus reducing the sorptive capacity.

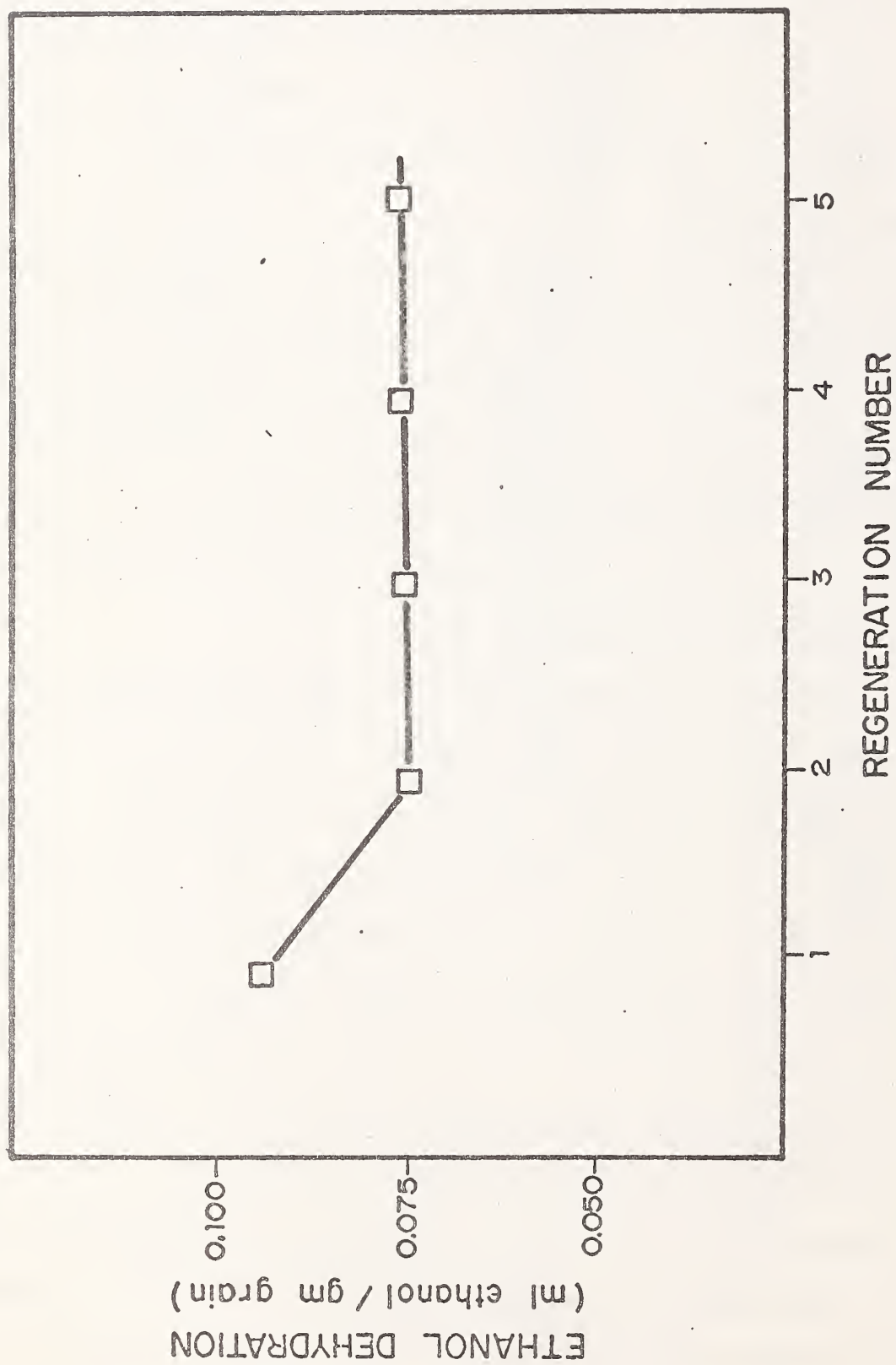


Figure 16. Ethanol Dehydration Capacity vs. the Number of Regenerations for 99 wt% Ethanol

## General Observations About the Process

As the experiments were being run several insights were developed relative to the use of adsorption for the dehydration of ethanol. One concerned the mechanism of the process itself and the other indicated that process modifications would be required to increase ethanol recovery. These were grouped as follows:

adsorption versus absorption

ethanol sorption

### Adsorption versus absorption

Figure 17 shows a profile of effluent sample concentration vs. time for a typical run. Note that at the beginning of the run, the initial effluent concentration was in the 99 to 100 wt% range and dropped off very fast after about 100 minutes and decreased very slowly after approximately 220 minutes. At this point, the effluent concentration was still 5 wt% above the inlet feed concentration. A possible explanation for this is that water and ethanol were adsorbed onto the surface of the barley very quickly and then the adsorbed water and ethanol were slowly absorbed into the cells of the barley, consequently making more surface available for further adsorption. According to this theory, water and ethanol would be removed very quickly from the feed stream by adsorption until all of the available barley surface was covered. At this point, the effluent ethanol concentration would decrease because water could no longer be removed from the feed at a fast enough rate. The slower absorption process would predominate and slowly make more surface available for adsorption. Therefore, the adsorption process would then occur at a much slower rate. Water would be removed from the feed stream at a rate just fast enough to keep the effluent ethanol concentration a few percentage points above that of the entering feed.

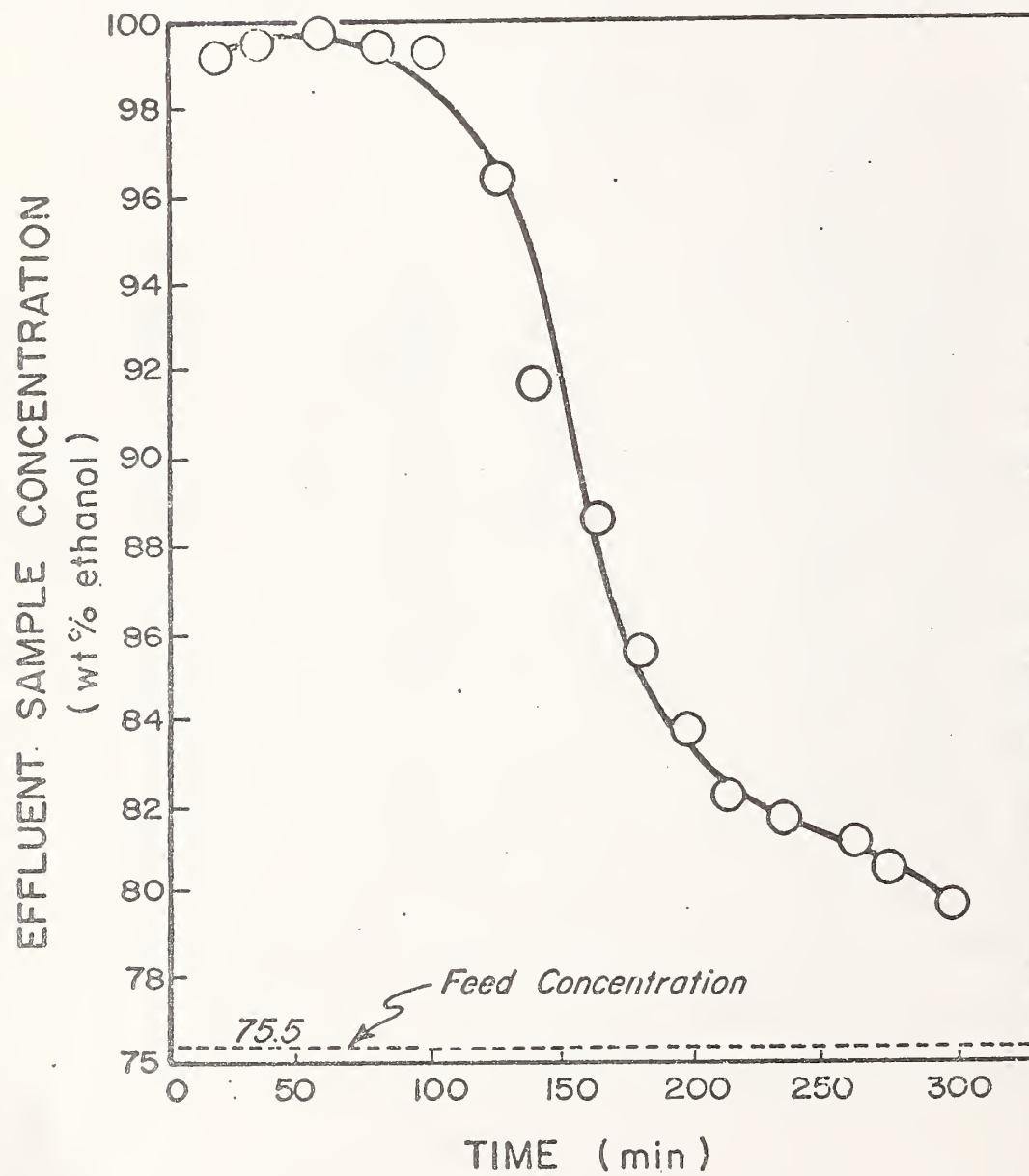


Figure 17. Effluent Ethanol Concentration vs. Time



Since barley cells normally contain water and the barley was desiccated before each run to remove this water, it seems reasonable to assume water would re-enter these cells during the run by the process described above. Earlier researchers developed an equation to describe isotherms for water sorption by wheat which was based on essentially the same ideas as were discussed above and they obtained very good correlation with the data from a number of investigators.

### Ethanol sorption

Although water was primarily sorbed by the grain some ethanol was also removed from the feed stream. Calculations indicated that throughout the runs 3-35 wt% of the ethanol was removed from the feed stream by grain sorption. As previously mentioned these percentages are only approximate due to the assumptions required for their calculation, and no correlation with process variables was apparent. However, it is apparent that efficient ethanol recovery will require that the ethanol be recovered from the sorbate and the grain. This will be further discussed in the Recommendations section of this report.

## SUMMARY AND RECOMMENDATIONS

A summary of the experimental adsorption results, their application to the design of a farm-scale unit, and the energy consumption for this method of ethanol dehydration will be addressed in this section.

### Summary of Experimental Results

Experimental studies have shown that:

1. The use of barley grain as an adsorbant is a feasible method for producing 99 wt% ethanol.

2. Over the ranges of the variables studied in this investigation, a reasonable dehydration capacity for 99 wt% ethanol from dry barley was 0.06 ml ethanol/gm barley (0.0072 gal ethanol/lb barley).
3. Regeneration of the barley for multiple use as an adsorbant reduced its dehydration capacity by about 20%.
4. Enough ethanol was adsorbed along with the water so that it should be recovered; therefore, the liquid removed from the barley during regeneration should be sent back to the distillation column.

The effects of the process variables can be summarized as follows:

1. The water adsorption capacity of the barley grain was fairly constant:
  - a. the capacity was independent of the ethanol-water feed composition over a range of 55-87 wt% ethanol.
  - b. the capacity decreased in proportion to the initial water content of the barley over a 0-2.4 wt% range.
2. An increase in barley grain temperature decreased its adsorption capacity; this temperature effect was a function of the initial grain temperature, feed mass flux, and adsorber geometry:
  - a. as the initial grain temperature was increased from 86°C to 103°C the capacity decreased; the decrease was much larger at low feed mass fluxes than high.
  - b. the adsorption process generated heat but at low mass fluxes (less than 1 gm/min-cm<sup>2</sup>) so little heat was generated that it could be dissipated to the surroundings from the adsorber and had little effect on capacity.
  - c. at feed mass fluxes of 0.1-0.34 gm/min-cm<sup>2</sup> the capacity decreased because the temperature of the column increased as heat was generated faster than it could be dissipated from the adsorber.

- d. as the adsorber diameter was increased from 0.75" to 2.5" in the capacity decreased because the volume increased faster than the surface area; therefore, for a given adsorber length, the heat generation increased faster than the surface area available to dissipate heat to the surroundings and the temperature increased.
  - e. for a given adsorber diameter an increase in length had little effect on capacity because the ratio of volume to surface area did not change.
- 3. The 1/32" hammer-milled grain had a little more adsorption capacity than the 1/16" and 1/8" which were very similar; however, the 1/32" is not recommended because it would require more grinding energy and would increase the pressure drop of the feed through the adsorber.
  - 4. Straw did not have as much capacity as grain and would be more difficult to grind.

#### Farm-scale Adsorber

Two limitations existed when the farm-scale adsorber was designed:

- 1. Because a farm-scale adsorber will be much larger than the equipment used in this investigation, the dehydration capacity may be smaller due to the increased temperatures that could occur with larger-diameter adsorbers.
- 2. The concept of grain regeneration was evaluated but no experiments were conducted to collect design information. Therefore, the design of the regeneration equipment was not based on experimental data.

For the above reasons it must be recognized that the performance of the following farm-scale adsorber will not be exactly the same as that of the smaller equipment used to collect experimental data.

### Design basis

A production rate of 1 gal/hr of 99 wt% ethanol was selected as the basis for the farm-scale unit. This overcomes the difficulty of trying to decide what size constitutes farm-scale, and provides a convenient base for facilities larger than 1 gal/hr. For example, a production rate of 10 gal/hr would require ten adsorbers, ten times as much preheater area, etc. A schematic of the farm-scale unit is shown in Figure 18. It was assumed that the feed to the adsorber would be 12.5 lb/hr of distillate vapor that is 75 wt% ethanol and 25 wt% water.

### Adsorption system

As shown in Figure 18 the adsorption system consists of a preheater, an adsorption column, and a product condenser.

The purpose of the preheater is to heat the distillate vapor from about 74°C to about 86°C and to compensate for heat losses in transferring the distillate from the distillation column to the adsorption column. Heat is provided by the bottoms liquid from distillation which has a temperature of about 96°C. The surface area of the preheater should be 5 ft<sup>2</sup> and the bottoms liquid flow rate should be 16 lb/hr (20% of the total bottoms flow rate). All piping between the distillation column and the adsorption column should be well insulated.

The adsorption column should be 10 in. in diameter by 10 ft. - it could be fabricated from aluminum irrigation pipe. It will hold about 4-1/4 bu of barley which is ground in a hammer mill with a 1/8" screen. The feed mass flux is about 0.2 gm/min-cm<sup>2</sup> which is well within the range of this experimental investigation. About 20% excess capacity has been provided to compensate for some of the uncertainty caused by going from a 2 1/2"-diameter experimental column to a 10" diameter farm-scale column. Some insulation will probably be required because the grain in the column should be dry and close to 86°C when



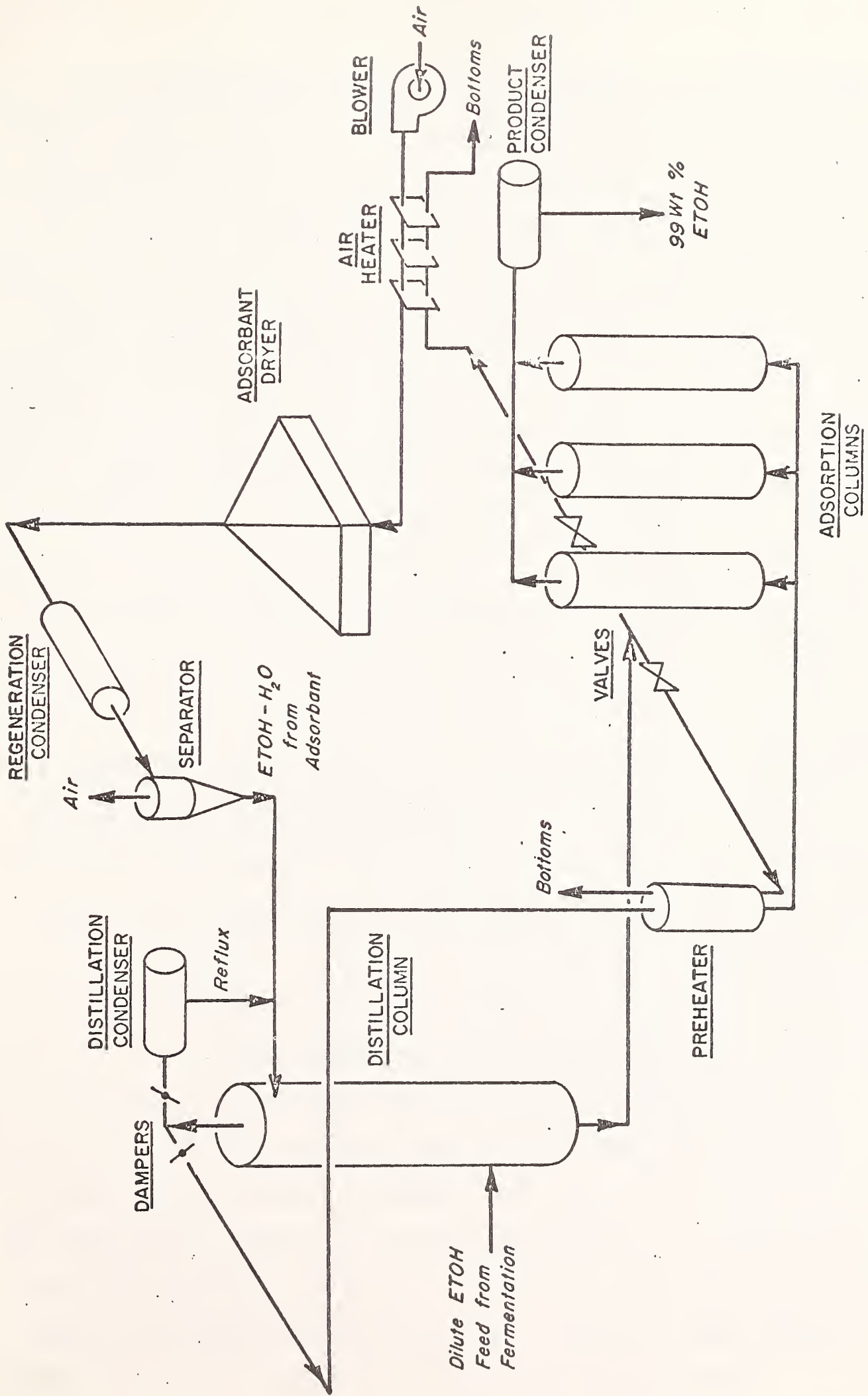


Figure 18. Process Schematic for Ethanol Dehydration Using Barley Adsorption

the vapor is fed into it; however, too much insulation might result in an excessive temperature increase due to the heat of adsorption. Insulation one-inch thick would be good to start with and it could be altered depending on the performance of the column. Because this column only can dehydrate one gallon of alcohol, multiple adsorption columns will be required if larger quantities are desired. The multiple columns will provide the opportunity to regenerate a column while the other(s) are being used for adsorption (this will be discussed in the next section). It should be noted that eventually the grain will lose its adsorbent properties and can then be fermented to produce ethanol; fermentation of the grain will produce about seven times as much alcohol as it can dehydrate by adsorption.

The product condenser can be air-cooled and should have a surface area of about 5 ft<sup>2</sup>.

### Regeneration system

A regeneration or drying system will be required because (1) the grain for adsorption must be dried prior to its initial use and (2) the grain must be regenerated for multiple use (if the grain was only used once for adsorption and then fermented there would be about seven times as much alcohol produced as could be dehydrated).

It would be desirable to keep the grain in the adsorption column during regeneration. However, this approach does not appear feasible for a farm-scale unit. At first glance it would appear hot air could be used to regenerate the grain in situ; however, because of the small grain size and length of the column the pressure drop would be quite high. Therefore, instead of being able to use an inexpensive blower, an air compressor would be required. The compressor could not be oil-lubricated because the oil would be carried into the adsorption column and foul up the grain. A second possibility would avoid using a

compressor - it is based on the decrease of grain adsorption capacity as the temperature is increased. Perhaps a second stream of distillate vapor could be heated to a high temperature and directed to the adsorption column requiring regeneration; this high-temperature distillate might strip the adsorbed water and ethanol from the grain and the total effluent could be condensed and fed back to the distillation column in the reflux stream. This latter regeneration method is appealing but cannot be evaluated without experimental data.

Therefore, the recommended regeneration system involves removing the grain from the adsorption column. The additional handling of the grain to remove it from the adsorption column, dry it, and then repack the column is undesirable but provides a reliable method of regeneration. It consists of a blower, air heater, adsorbant dryer, regeneration condenser, and separator (Figure 18).

The blower should have a capacity of  $1,000 \text{ ft}^3/\text{min}$  at a static pressure of  $5" \text{ H}_2\text{O}$ . It would be desirable to heat the air as high as possible using the remaining 80% (64 lb/hr) of the bottoms liquid ( $96^\circ\text{C}$ ) from the distillation column. About  $60 \text{ ft}^2$  of total preheater surface area should be installed. This should be divided into at least three heating coils with the bottoms liquid and air flow countercurrent, i.e., the coolest liquid should be heating the coolest air and the hottest liquid heating the hottest air (Figure 18).

The adsorbant dryer was based on limiting the depth of grain in the bed to 4 in. - this gives a dryer area of  $16 \text{ ft}^2$ . The grain would be supported on a steel mesh screen and the air introduced into a space or plenum below the screen. The dryer must have a hood to recover the adsorbed ethanol that will be removed from the grain along with the water.

The purpose of the regeneration condenser and separator is to remove the ethanol and water from the air. The condenser could be air-cooled and would require about  $75 \text{ ft}^2$  of surface area. The separator could be a vertical drum 2 ft. in diameter and 5 ft. high with the inlet 2 ft. from the bottom.

Because of (1) the extra time required to handle the grain and (2) absence of experimental drying data, the total regeneration time cannot be estimated. The ideal situation would occur if the total regeneration time was equal to or less than the adsorption time. This would require only two columns for a continuous ethanol production rate of 1 gal/hr - a regenerated adsorption column would be available at the beginning of each hour. If the regeneration time exceeds the adsorption time, more than two columns will be required for continuous dehydration.

### Energy Consumption

It was not necessary in this investigation to make detailed calculations to prove that adsorption dehydration of ethanol provides a net positive energy balance. This had previously been done by M. E. Ladisch and K. Dyck in an article "Dehydration of Ethanol: New Approach Gives Positive Energy Balance" (Science, Vol. 205, August 31, 1979, pp. 898-900). They had done some preliminary experiments using corn and cellulose as an adsorbent and shown that the ratio of the combustible energy of the dehydrated ethanol to the energy required to separate it from the dilute beer produced by fermentation exceeded 10:1. They assumed that distillation increased the ethanol from 12 wt to 84.8 wt% and in this study it was assumed the increase was from 10 wt% to 75 wt%. Therefore, the energy balance should be comparable and shows the desirability of adsorption dehydration of ethanol.





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